



## Solar nano-photocatalytic pretreatment of seawater: Process optimization and performance evaluation using response surface methodology

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The critical challenge for the cost-effective application of seawater reverse osmosis systems is membrane fouling due to organic pollutants. This study evaluates the effectiveness of employing solar photocatalysis of TiO<sub>2</sub>-ZnO process to pretreat reverse osmosis (RO) feed seawater under solar irradiation. Process optimization and performance evaluation were undertaken using the central composite design (CCD) with response surface methodology (RSM) techniques. Statistical analysis was performed to determine the interactive relationships and effects between input factors such as TiO<sub>2</sub> dosage, pH, reaction time (RT) and ZnO dosage. Process optimization and performance evaluation were determined in terms of degradation efficiency of total organic carbon (TOC) and chemical oxygen demand (COD). The quadratic models developed for TOC and COD responses were found to be significant with very low probabilities (< 0.0001). Organic removal with a reaction time of 90 min, pH 4.0, TiO<sub>2</sub> dosage of 0.6 g L<sup>-1</sup> and ZnO dosage of 0.39 g L<sup>-1</sup> were found to be optimum by achieving 60.97% degradation of COD and 64% degradation of TOC. The experimental results (COD removal = 58.09% and TOC removal = 62.25%) correspond well with the predictions. The optimum validation degradation efficiencies without changing original pH of seawater (at pH = 8) were obtained as: COD removal = 51.23% and TOC removal = 59.65%.

Keywords: Seawater, reverse osmosis (RO) membrane fouling, solar nano-photocatalysis, central composite design, response surface methodology (RSM).

### Introduction

Increasing requirement for safe water supply, due to industrial development and population growth, has led to water stress and deterioration of freshwater resources. Rigorous efforts are ongoing to prevent this crisis by conserving existing freshwater resources and converting abundantly available seawater using cost-effective desalination technologies<sup>1</sup>. Among other desalination technologies, reverse osmosis (RO) process is widely employed to reclaim clean water from seawater and industrial wastewater in many parts of the world. However, the seawater reverse osmosis (SWRO) industries encounter critical challenges due to membrane fouling and high organic loading<sup>2</sup>. Therefore the degradation of organic pollutants from RO feed seawater is a major challenge to enhance the performance and efficiency of SWRO systems.

An ultraviolet driven photocatalytic pretreatment can be employed for the degradation of humic substances (higher molecular organics) and microorganisms present in the feed water<sup>3</sup>. The energy generated from the photocatalytic reaction breaks down the humic substances and also kills microorganisms, thereby eliminating the primary source for membrane fouling<sup>4</sup>. UV photo-oxidation uses ultraviolet light to activate a catalyst to physically decompose the organic matter into non-toxic components. The degradation of organic compounds in the presence of UV light is a slow process, (reaction rates are slow) and hence not suitable for large scale industrial applications. To enhance the reaction rates, several catalysts such as hydrogen peroxide, ozone, Fe(II), titanium dioxide, zinc oxide, etc. are used in these types of reactions.

Remediation of organic pollutants using photocatalysts

is directly linked to the generation of hydroxyl radicals<sup>5</sup>. Hydroxyl radicals are powerful oxidising species that can attack organic pollutants to degrade the contaminants into mineral acids, H<sub>2</sub>O and CO<sub>2</sub><sup>6</sup>. One of the research works<sup>7</sup> have demonstrated the application of UV/TiO<sub>2</sub> photocatalysis for disinfecting seawater, where the organics are degraded using immobilized TiO<sub>2</sub>. Another study<sup>8</sup> enhanced photocatalytic reaction for decontaminating phenol in seawater using TiO<sub>2</sub> based catalysts under weak UV light irradiation.

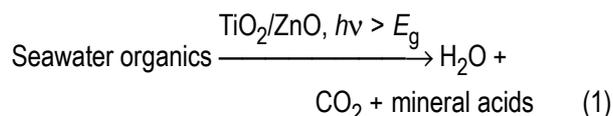
Seawater organic degradation by photocatalysis is challenging due to the salinity effect and electron scavenging issues. However, various past research studies have demonstrated improved results in overall organic removal efficiency. Despite the effect of salinity, one of the research works<sup>9</sup> proved the superiority of UV/TiO<sub>2</sub> among other technologies for treating marine water in the ballast water application. One of the research studies<sup>10</sup> applied ZnO modified TiO<sub>2</sub> nanocomposites for organic pollutant removal from feedwater and reported enhanced degradation performance compared to pure TiO<sub>2</sub>. The photodegradation efficacy of TiO<sub>2</sub> can be improved by preventing the high rate of electron-hole recombination. Since ZnO exhibits high electron mobility, lower electron-hole recombination can be achieved by using ZnO-TiO<sub>2</sub> in combination<sup>11</sup>. Moreover, the hydroxyl radicals, mainly responsible for organic degradation, are found to be overly generated due to the interactive catalytic effect of TiO<sub>2</sub>-ZnO hybrid system. The synergistic effect in TiO<sub>2</sub>-ZnO combination is due to the improvement of charge transfer resulting in a larger production of hydroxyl radicals<sup>12</sup>.

In the present study of seawater photocatalyst-oxidation treatment, membrane-fouling-organic-contaminants are degraded using ZnO-TiO<sub>2</sub> catalysts under solar irradiation. The operational conditions to achieve optimum degradation of chemical oxygen demand (COD) and total organic carbon (TOC) were evaluated. Photocatalytic degradation technology is widely applied in treating different types of wastewater and industrial effluents. However, very few research studies attempted its application in treating seawater, specifically for mitigating RO membrane fouling due to organic contaminants. Optimization of TiO<sub>2</sub>-ZnO-solar photocatalytic degradation of organics from seawater using renewable solar energy is still not available as per the knowledge of present research group. The number of studies dealing with the ap-

plication of RSM optimization and solar-nano ZnO-TiO<sub>2</sub>-photocatalysis for the degradation of organics from seawater is very sparse and here lies the novelty of the present research work.

## Results and discussion

Table 1 shows the central composite design layout and the respective response values generated from each experimental run. The COD degradation percentage found to range from 28.13% to 58.64% while the TOC removal lies between 36.82% to a maximum of 65.86%. Based on experimental response values obtained in each run, the removal of TOC and COD are calculated as a percentage of initial values and used in RSM modeling and optimization. In the solar photocatalytic reaction of seawater organics, organic compounds are degraded to mineral acids, H<sub>2</sub>O and CO<sub>2</sub>. The photo mineralization with the degradation of organic degradation undertaken in seawater solution is demonstrated in the eq. (1).



where  $E_g$  is the bandgap energy of the semiconductor photocatalyst and  $h\nu$  is the solar irradiation.

### RSM models of actual and coded factors:

In the current study, analysis of variance (ANOVA) technique is used to determine the significance of the input factors on the output responses. As per ANOVA results, COD and TOC models were found to be significant by F-test at 95% confidence level (Prob < 0.05). Table 2 shows the ANOVA regression model equations of TOC and COD removal in actual and coded factor terms. Coded factor models deliver a more expressive understanding of the process than equations represented in terms of actual factors. In coded factors, the terms are normalized and represented in relative weights while in equations with actual factors, owing to the presence of units, the importance of coefficients are incomparable. Making inference about the relative effect between process variables is possible from coded factors equations.

From the equations given in Table 2, it is clear that pH, RT, TiO<sub>2</sub> dose and ZnO dosage have first-order effects on

**Table 1.** The 4-factor central composite design matrix; input factors at actual levels and the experimental response results for solar nano-photocatalytic treatment of seawater

Run	Input factors				COD removal (%)		TOC removal (%)	
	A: TiO <sub>2</sub> (g L <sup>-1</sup> )	B: ZnO (g L <sup>-1</sup> )	C: pH	D: RT (min)	Experimental	RSM- predicted	Experimental	RSM- predicted
1	0.3	0.6	8	90	46.45	48.01	39.31	39.01
2	0.6	0.6	8	90	48.45	48.97	48.95	47.84
3	0.45	0.45	6	135	58.64	54.73	48.43	45.38
4	0.3	0.3	4	90	44.54	46.43	65.86	63.95
5	0.45	0.45	8	135	51.53	52.16	54.39	52.89
6	0.3	0.3	8	180	28.13	28.65	45.58	44.38
7	0.45	0.6	6	135	43.83	44.74	39.05	37.42
8	0.6	0.3	8	90	41.12	39.16	36.82	36.62
9	0.3	0.3	4	180	45.54	43.81	57.86	58.76
10	0.6	0.3	4	180	49.58	51.69	55.64	56.15
11	0.45	0.45	6	135	56.45	54.73	42.46	45.38
12	0.45	0.45	6	135	56.45	54.73	47.87	45.38
13	0.45	0.45	6	90	52.85	56.04	38.56	43.08
14	0.3	0.6	8	180	46.45	45.39	53.18	53.42
15	0.6	0.45	6	135	52.85	56.94	44.49	46.94
16	0.3	0.3	8	90	32.43	31.28	37.64	39.22
17	0.3	0.6	4	90	42.25	43.14	41.43	40.94
18	0.45	0.45	6	135	52.85	54.73	47.72	45.38
19	0.6	0.6	4	90	44.28	44.1	47.84	49.78
20	0.3	0.45	6	135	52.85	52.52	42.11	43.82
21	0.45	0.45	6	135	57.45	54.73	45.13	45.38
22	0.6	0.6	8	180	47.45	46.35	59.51	62.25
23	0.45	0.45	6	135	58.21	54.73	50.76	45.38
24	0.3	0.6	4	180	41.25	40.51	43.45	45.01
25	0.45	0.3	6	135	38.32	41.48	37.05	38.68
26	0.6	0.6	4	180	42.28	41.48	56.78	53.84
27	0.6	0.3	4	90	58.54	54.32	62.41	61.34
28	0.45	0.45	4	135	55.17	57.3	59.55	61.05
29	0.45	0.45	6	180	51.45	53.42	46.29	47.69
30	0.6	0.3	8	180	35.15	36.54	42.02	41.77

**Table 2.** Final ANOVA regression model equations for COD and TOC responses in terms of actual and coded factors

	Coded factors equations	Actual factors equations
COD removal (%)	= + 54.73 + 2.21×A + 1.63×B – 2.57×C – 1.31×D – 1.73×A×B + 5.01×B×C – 11.62×B <sup>2</sup>	= – 20.20 + 49.35×TiO <sub>2</sub> + 409.97×ZnO – 8.79×pH – 0.029×RT – 76.91×TiO <sub>2</sub> ×ZnO + 16.68×ZnO×pH – 516.25×ZnO <sup>2</sup>
TOC removal (%)	= + 45.38 + 1.56×A – 0.63×B – 4.08×C – 2.31×D + 2.86×A×B + 5.7×B×C + 2.31×B×D + 2.59×C×D – 7.33×B <sup>2</sup> + 11.59×C <sup>2</sup>	= + 207.38 – 46.81×TiO <sub>2</sub> + 71.54×ZnO – 49.23×pH – 0.275×RT + 127.11×TiO <sub>2</sub> ×ZnO + 18.99×ZnO×pH + 0.34×ZnO×RT + 0.028×pH×RT – 325.76×ZnO <sup>2</sup> + 2.89×pH <sup>2</sup>

COD degradation along with quadratic-effect of ZnO dose and interaction effect among (pH)(ZnO) and (TiO<sub>2</sub>)(ZnO).

While from TOC degradation equation it can be seen that ZnO and pH has a second-order influence on the response.

The negative coefficient of factor C: pH in both response equations show that increase in its value from -1 to +1 (from pH = 4 to pH = 8) will decrease the degradation rate. This is in agreement with the optimum conditions obtained where pH value for optimum degradation was found to be 4.

*Process optimization and performance evaluation:*

The RSM-numerical optimization technique is used to optimize multiple responses in order to achieve maximal removal efficiencies of TOC and COD simultaneously. This approach enables to locate the optimal settings of the variables to attain the desired response. According to the numerical optimization steps in the software the desired goal for input variables (TiO<sub>2</sub>, ZnO dosages, pH and RT) are chosen as 'in range' while TOC and COD removal responses are defined as 'maximum'. The software combines the indi-

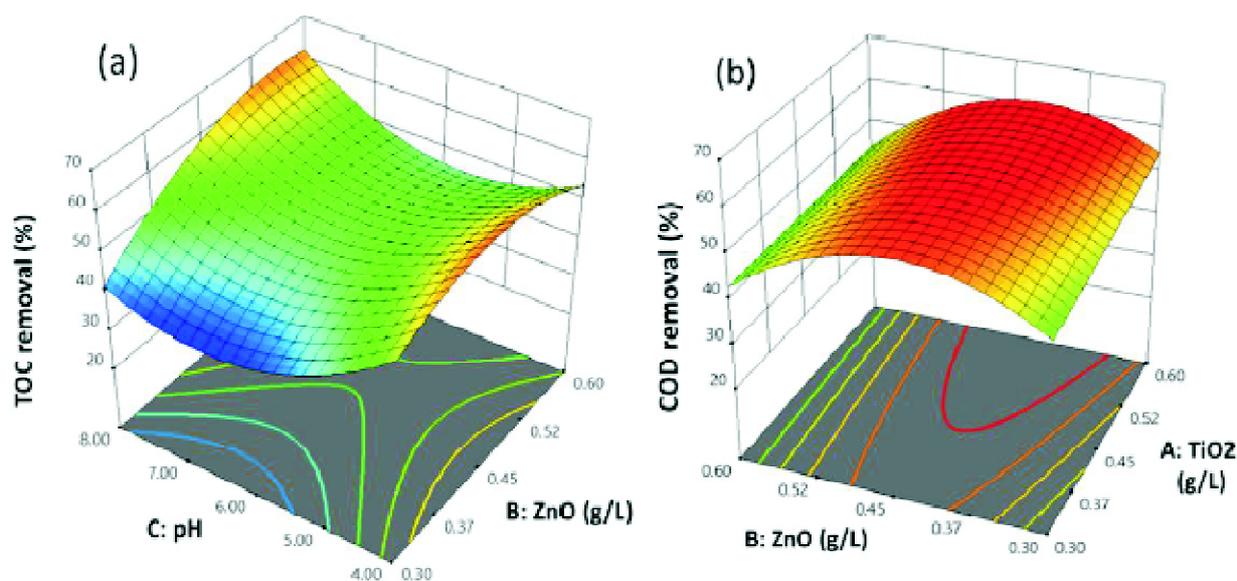
vidual desirability to determine the best set of trade-offs. The program then searches the design space to optimize desirability function based on the defined goals. Table 3 shows the values of optimum removal efficiencies forecasted by the model under optimum process operating conditions. Numerical optimization was also conducted by keeping 'target pH = 8'. The results obtained at this setting enable to operate the photocatalytic pretreatment of seawater, without altering its original pH. Additional experiments are performed to confirm the validity of the prediction, revealing good agreement between predicted and experimental results.

*Effects of input factors as 3-D response surfaces:*

Figs. 1(a,b) show the 3-D response surface plots for TOC and COD removal obtained by statistical analysis through Design-Expert software. The plots demonstrate the effects

**Table 3.** Optimum COD and TOC degradation efficiencies and experimental validation results at optimum conditions (for seawater pH in the range from 4 to 8 and at target pH = 8)

Responses	Optimum solution	Experimental validation	Optimum condition
COD removal (%)	60.97	58.09	TiO <sub>2</sub> dosage = 0.6 g L <sup>-1</sup> , ZnO dosage= 0.39 g L <sup>-1</sup> , pH = 4, RT = 90 min
TOC removal (%)	64.02	62.25	
COD removal at pH = 8	53.05	51.23	TiO <sub>2</sub> dosage = 0.6 g L <sup>-1</sup> ,
TOC removal at pH = 8	62.35	59.65	ZnO dosage = 0.51 g L <sup>-1</sup> , pH = 8, RT = 180 min



**Fig. 1.** (a) 3-D surface plot for TOC removal versus pH and ZnO dosage at optimum setting of TiO<sub>2</sub> dosage = 0.6, reaction time (RT) = 180.0 min, (b) 3-D surface plot for COD removal versus ZnO dosage and TiO<sub>2</sub> dosage at optimum settings of pH = 4.0, reaction time (RT) = 90.0 min.

of two variables on the response when the other two variables kept constant at their optimum level. As observed in Fig. 1(b), the factor dosage has a linear effect on COD removal while the factor dosage has a quadratic effect. This second-order effect of factor is evident from the existence of term in the coded COD equation shown in Table 2. The non-linear effect of factor on TOC removal is evident from Fig. 1(a), where the maximum degradation occurred at pH = 4. The  $C^2$  term in the coded equation of TOC removal shown in Table 2 validates this quadratic behaviour.

*Effects of TiO<sub>2</sub> and ZnO dosages on overall photocatalytic degradation:*

In a redox photocatalytic reaction, charge transfer can be enriched when using TiO<sub>2</sub> in combination with ZnO. This, in turn, enhances the production of hydroxyl radicals. The efficiency of the photocatalytic treatment also depends on the ratio of TiO<sub>2</sub>/ZnO dosages, since excessive dosages increase the turbidity and hinder the sunlight required for the reactions. The preliminary experimental study has been conducted to determine the optimal and effective range of dosages, and the resulting combinations were used in experimental design (DOE). The 'AB' interaction term between factors A:TiO<sub>2</sub> and B: ZnO present in the coded equation in Table 2 shows their interaction effect on responses COD and TOC removal. The positive coefficient of 'AB' term in TOC-coded equation shows their synergistic effect while the negative coefficient in COD-coded equation shows the antagonistic effect. The synergistic effect in TiO<sub>2</sub>-ZnO combination is due to the improvement of charge transfer resulting in a larger production of hydroxyl radicals. In the present study, TiO<sub>2</sub> dosage of 0.6 g L<sup>-1</sup> and ZnO dosage 0.39 g L<sup>-1</sup> were found to be optimum by achieving 60.97% degradation of COD and 64% degradation of TOC. Similar catalysts dosage results were obtained in a previous TiO<sub>2</sub>-ZnO-aeration study conducted for petroleum wastewater organic degradation<sup>14</sup>. In our research work, an optimization study has also been conducted without changing the seawater pH. At original seawater pH = 8, TiO<sub>2</sub> dosage of 0.6 g L<sup>-1</sup> and ZnO dosage 0.51 g L<sup>-1</sup> have been found to be optimum, and 53.05% degradation of the COD and 62.35% degradation of the TOC is predicted. This results from the current study confirm that comparable TOC and COD degradation of seawater organic pollutants can be achieved without changing seawater pH.

*Effects of pH:*

The pH of the solution significantly affects the charge on semiconductor particles. The aggregate size and position of valence and conductance bands also depend on the pH of the reaction mixture. Optimum pH required for effective photocatalytic reaction varies from process to process due to the differences in intermediates formed. In the current study, the optimum pH required for maximum TOC and COD degradation has been determined as 4, while the initial average pH of the seawater before treatment has been determined as 8.08. On a commercial scale in SWRO plants, adjusting the pH of a larger volume of seawater to acidic (pH = 4) is not practical on a daily basis. Hence RSM numerical optimization study has been conducted keeping pH at 8 as the target and maintaining other factors in-range. Even though the initial optimum value suggested for pH is acidic (pH = 4), numerical optimization at target pH value (pH = 8) gave comparable results for TOC and COD removal.

As shown in Table 3, at the new setting of pH, organic removal with a reaction time of 180 min, pH of 8.0, TiO<sub>2</sub> dosage of 0.6 g L<sup>-1</sup>, ZnO dosage 0.51 g L<sup>-1</sup> have been found as optimum, and 62.35% removal of TOC and 53.05% removal of COD were predicted through numerical optimization techniques. The experimental validation results correspond well with the predictions (TOC = 59.65%, and COD = 51.23%). A similar range of pH was obtained in a research study<sup>15</sup> for seawater treatment using UV/TiO<sub>2</sub>. Moreover, the degradation efficiency of solar photocatalytic treatment does not depend on pH values range from 4 to 10<sup>16</sup>. Nevertheless, previous research studies show that slightly higher operational efficiency of photocatalysis can be achieved at acidic conditions when the pH values range from 2 to 6<sup>17</sup>.

From the RSM plot of TOC shown in Fig. 1(a), it is evident that the removal rate is slightly rising towards the acidic region with maximum degradation at pH value of 4. The enhanced inactivation under acidic pH is reported in the previous studies<sup>18</sup>. The negative coefficients of pH in coded equations for TOC and COD responses shown in Table 2 substantiate this argument. At pH less than optimal conditions, generation of (<sup>•</sup>OH) radicals become comparatively lower and lead to poor oxidation of organics. pH also affects the position of conductance and valence bands, size of catalyst agglomeration and the charge on catalyst particles<sup>19</sup>. The current study reveals that even though higher degradation of

TOC and COD occurs at low pH, comparable organic removal can be achieved without altering the original pH of the seawater.

*Effect of irradiation time:*

The optimum time required for seawater organic degradation is lower in TiO<sub>2</sub>/ZnO process, compared to the irradiation time required when any one of the catalysts employed independently. Irradiation time depends on the initial organic loading and the type of catalyst used. In the present study, the optimum irradiation time at the original pH of seawater (pH = 8) is obtained as 180 min. Similar irradiation time was reported in a research study, where the maximum organic removal is achieved in 170 min of solar photocatalytic treatment<sup>14</sup>. However, in the present study at acidic condition (at pH = 4), the optimum irradiation time was found to be 90 min. The lower irradiation time can be attributed to coulombic-force of attraction between positive surface-charge of both ZnO and TiO<sub>2</sub> catalysts (point of zero charge lies between 4.5 and 7 for both of the catalysts) and organic pollutants, which results in faster degradation.

**Experimental**

*Materials and methods:*

The seawater samples were characterised before the treatment to determine COD, pH, salinity, dissolved oxygen (DO) and TOC. The mean values (before treatment) of COD, pH, salinity, DO, and TOC of the seawater samples were determined as 5.12 mg/L, 8.08, 33960 mg/L, 5.38 mg/L, and 3.65 mg/L respectively. The photocatalysts used were nano zinc oxide (ZnO, 99.9% pure, APS: 20 nm), purchased from mkNANO, Canada and titanium dioxide (TiO<sub>2</sub>) Aeroxide P-25 supplied by Evonik Industries, Germany. NaOH and HCl were used for adjusting the pH of the solution as per the settings prescribed by the CCD matrix (Table 1). Chemical oxygen demand (COD) test was done by using COD HR+ (01–15000 ml/L) reagent purchased from CHEMetrics. Total organic carbon (TOC) of each sample was analysed by using TOC Analyzer (LCSH/CSN) procured from SHIMADZU Japan. All the samples were filtered before TOC/COD analysis, using 0.22 m Millipore Durapore membrane (150 mm-diameter and Ashless-40). Solar radiant flux in the region was measured using KIPP and ZONEN-CMP 21 Pyranometer and found to be 680±4 Watts/m<sup>2</sup>. All experiments were carried out from 11 AM to 2 PM to ensure the availability of

maximum UV radiation during photocatalytic reactions.

*Experimental procedure:*

The experimental setup of TiO<sub>2</sub>-ZnO solar nano photocatalytic includes a photo-reactor, a peristaltic pump for recirculation of seawater through photoreactor, a recirculation tank (4.5 litres) subjected to stirring with magnetic stirrers and an aeration pump. The photoreactor consists of nine borosilicate glass tubes (650 mm length, 22 mm inner diameter and 2 mm thickness) connected in parallel used for seawater recirculation exposed to solar irradiation. Seawater solution runs through the tubular photocatalytic reactor by means of peristaltic pumps at a flow rate of 1.1 litres per minute, which is fixed for all experiments. The pH of the solution was varied from 4 to 8 as per the factor settings of each run prescribed by central composite design (CCD). Samples were taken for TOC/COD analysis at respective reaction time interval settings varied from 90 min to 180 min. The tilt of the reactor is fabricated adjustable (19 to 24° angle with horizontal) to make it align with solar-angle and being conformable to the location latitude (23°40'12.97" N). Parabolic reflectors were installed beneath the reactor tubes to make the solar irradiation to be reflected and diffused to the tubes at optimum intensity. The magnetic stirring and recirculation using a peristaltic pump ensure proper mixing and sufficient supply of oxygen required for organic degradation. The post-separation of the catalysts is performed by overnight sedimentation process in a settling tank. The settling time can be accelerated either by adding a coagulant (like basic aluminium chloride) or by changing the pH to the point of zero charge (pH<sub>pzc</sub>) for surface charge neutralisation and thereby enhancing the aggregation and sedimentation process<sup>20</sup>.

*Design of experiments and statistical analysis:*

RSM modeling and optimization studies were carried out using Design Expert (version 11, Stat-Ease, USA) software. Response surface methodology is a statistical tool utilising experimental data generated from respective central composite design (CCD) to optimize and model any system in which the response variable under study is affected by key input variables<sup>21</sup>. RSM is a promising technique for process optimization, strategically calculating optimum condition for a multivariate process<sup>22</sup>. This technique helps to establish relationships between response variables and controllable input variables or process factors. In the current study, ZnO

dosage, TiO<sub>2</sub> dosage, reaction time and pH were chosen as input parameters for seawater organic degradation and their +1 and -1 level was set at 0.3 and 0.6 g L<sup>-1</sup>, 0.3 and 0.6 g L<sup>-1</sup>, 90 and 180 min and 4 and 8, respectively. The efficiency of the photocatalytic treatment is analysed in terms of degradation of COD and TOC. For evaluating the influence of catalyst ratio on the overall organics degradation, five different TiO<sub>2</sub>-ZnO ratios (i.e. 0.5, 0.75, 1, 1.25 and 1.5) were tested in the preliminary experimentation. TOC and COD removal rate were examined by varying ZnO dosages (0.9, 0.6, 0.45, 0.36 and 0.3 g L<sup>-1</sup>) while keeping TiO<sub>2</sub> concentration fixed at 0.45 g L<sup>-1</sup>. Since maximum TOC/COD removal rate was observed at the equal proportion of catalysts, (ratio = 1), an equal amount of dosages were used for both TiO<sub>2</sub> and ZnO in the CCD factor settings (0.3 g L<sup>-1</sup> and 0.6 g L<sup>-1</sup> as -1 and +1 ranges respectively).

CCD is one of the RSM techniques well suited for fitting a quadratic curve in order to optimize significant process parameters by conducting the minimum number of experiments. This second-order design technique works well for process optimization, as well as to analyse interdependence between parameters<sup>23</sup>. In the present study, 30 experimental runs were conducted using CCD design. TOC and COD degradation were treated as responses or dependent variables. Performance and treatment efficiency is evaluated by analysing the percentage removal of TOC and COD responses. Each independent process factor is varied between -1 and +1 at predetermined ranges calculated from preliminary experimentation. One factor at a time (OFAT) analysis was conducted to find the levels of input variables, and for determining process design space consists of suitable factor ranges. The TOC and COD percentage degradation obtained from OFAT analysis were found to be less than that resulted from RSM analysis (53% and 49% against 64% and 60.97%). This shows that the study on interaction or interdependence of influencing factors is very important in a multivariate system. The synergistic or antagonistic effects of input factors on responses are not visible in the univariate investigation of OFAT analysis of any process. Solar photocatalytic seawater treatment is a complex multivariate process in which the system performance and organic removal efficiency are affected by a large number of parameters. Therefore, multivariate optimization strategies are necessary to evaluate the optimum operating conditions.

## Conclusions

In this study, treatment efficiency and performance evaluation for advanced oxidation of TOC and COD degradation from seawater have been investigated. Statistical response surface methodology (RSM) was applied to assess the interaction among key process factors such as ZnO-TiO<sub>2</sub> dosages, reaction time (RT) and pH to determine the treatment efficiency and optimum operational settings. Regression models obtained for both TOC and COD responses were found to be significant with the lowest probability (< 0.0001). The removal with a reaction time of 90 min, pH of 4.0, TiO<sub>2</sub> dosage of 0.6 g L<sup>-1</sup> and ZnO dosage of 0.39 g L<sup>-1</sup> were found to be optimum and overall degradation of 64.02% of TOC, and 60.97% of COD were accomplished. The optimum prediction corresponds well with validation-experimental results (62.25% for TOC and 58.09% for COD removal). The optimum validation degradation efficiencies for COD and TOC removal without changing the original pH of seawater (at pH = 8) were obtained as 51.23% and 59.65% respectively. Hence the optimization analysis results from this study confirm that comparable organic degradation can be achieved without altering the original pH of seawater. The synergistic degradation efficiency obtained in this work depicts that the support of TiO<sub>2</sub> catalyst with ZnO can be a feasible alternative for persistent organic removal. Hence the solar supported photocatalytic pretreatment of seawater can be applied as a sustainable technique for degradation of RO membrane fouling organic pollutants. The solar nano-photocatalysis of TiO<sub>2</sub>-ZnO is a unique method for decontaminating highly saline seawater by utilising efficient renewable resources.

## References

1. A. Matin, Z. Khan, S. M. J. Zaidi and M. C. Boyce, *Desalination*, 2011, **281**, 1.
2. J. N. Hakizimana, B. Gourich, C. Vial, P. Drogui, A. Oumani, J. Naja and L. Hilali, *Desalination*, 2016, **393**, 90.
3. M.-J. Kim, K.-H. Choo and H.-S. Park, *J. Photochem. Photobiol. A: Chem.*, 2010, **216**, 215.
4. Z. Xu, T. Wu, J. Shi, K. Teng, W. Wang, M. Ma, J. Li, X. Qian, C. Li and J. Fan, *J. Memb. Sci.*, 2016, **520**, 281.
5. T. Aissani, I. Yahiaoui, F. Boudrahem, S. Ait Chikh, F. Aissani-Benissad and A. Amrane, *Sep. Sci. Technol.*, 2018, **53**, 1423.
6. S. Mortazavian, A. Saber and D. E. James, *Catalysts*, 2019, **9**.
7. D. Rubio, J. F. Casanueva and E. Nebot, *J. Photochem. Photobiol. A: Chem.*, 2013, **271**, 16.
8. T. Wang, Z. Y. Xu, L. G. Wu, B. R. Li, M. X. Chen, S. Y. Xue, Y.

- C. Zhu and J. Cai, *RSC Adv.*, 2017, **7**, 31921.
9. J. Moreno-Andrés, L. Romero-Martínez, A. Acevedo-Merino and E. Nebot, *Sci. Total Environ.*, 2017, **581**, 144.
10. T. Yang, J. Peng, Y. Zheng, X. He, Y. Hou, L. Wu and X. Fu, *Appl. Catal. B: Environ.*, 2018, **221**, 223.
11. R. Qin, F. Meng, M. W. Khan, B. Yu, H. Li, Z. Fan and J. Gong, *Mater. Lett.*, 2019, **240**, 84.
12. I. J. Ani, U. G. Akpan, M. A. Olutoye and B. H. Hameed, *J. Clean. Prod.*, 2018, **205**, 930.
13. A. R. Khataee, M. Fathinia, S. Aber and M. Zarei, *J. Hazard. Mater.*, 2010, **181**, 886.
14. D. A. D. A. Aljuboury, P. Palaniandy, H. B. A. Aziz, S. Feroz and S. S. A. Amr, *Water Sci. Technol.*, 2016, **74**, 1312.
15. D. Rubio, J. F. Casanueva and E. Nebot, *J. Photochem. Photobiol. A: Chem.*, 2013, **271**, 16.
16. S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco and W. Gernjak, *Catal. Today*, 2009, **147**, 1.
17. M. S. M. Muruganandham, *Dye. Pigm.*, 2006, **68**, 133.
18. I. K. Konstantinou and T. A. Albanis, *Appl. Catal. B: Environ.*, 2004, **49**, 1.
19. S. Eydivand and M. Nikazar, *Chem. Eng. Commun.*, 2015, **202**, 102.
20. S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco and W. Gernjak, *Catal. Today*, 2009, **147**, 1.
21. S. Shojaei and S. Shojaei, *Int. J. Environ. Sci. Technol.*, 2018, 1.
22. G. K. Akkaya, H. S. Erkan, E. Sekman, S. Top, H. Karaman, M. S. Bilgili and G. O. Engin, *Int. J. Environ. Sci. Technol.*, 2019, **16**, 2343.
23. R. H. Meyers and D. C. Montgomery, "Response Surface Methodology: Process and Product Optimization Using Designed Experiments", John Wiley & Sons, Inc., 4th ed., 1995.
24. T. Karami, S. Elyasi and T. Amani, *Int. J. Environ. Sci. Technol.*, 2018, **15**, 2389.