Evaluating the TiO$_2$ as a solar photocatalyst process by response surface methodology to treat the petroleum waste water

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Abstract

The aim of this study is to investigate the performance of employing the solar photo-catalyst of TiO$_2$ to treat petroleum wastewater from Sohar oil Refinery (SOR), evaluate the performance of employing this process by a central composite design (CCD) with response surface methodology (RSM) and evaluate the relationships among operating variables such as TiO$_2$ dosage, pH, C$_0$ of COD, and reaction time to identify the optimum operating conditions. Quadratic models prove to be significant with very low probabilities (<0.0001) for the following two responses: total organic carbon (TOC) and chemical oxygen demand (COD).

TiO$_2$ dosage and pH are the two main factors that improved the TOC and COD removal while C$_0$ of COD and reaction time are the actual factors. The optimum conditions are a TiO$_2$ dosage (0.6 g/L), C$_0$ of COD (1600 ppm), pH (8), reaction time (139 min) in this method. TOC and COD removal rates are 15.5% and 48.5%, respectively. The predictions correspond well with experimental results (TOC and COD removal rates of 16.5%, and 45%, respectively). Using renewable solar energy and treating with minimum TiO$_2$ input make this method to be a unique treatment process for petroleum wastewater.

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Keywords: Petroleum waste water; Photo-catalyst of TiO$_2$; Advanced oxidation process (AOP); Response surface methodology (RSM)

1. Introduction

Nowadays, one of the major problems facing industrialized nations is contamination of the environment by hazardous chemicals. A wide range of pollutants compounds are detected in petroleum waste water in Sohar Oil Refinery, so, the elimination of these chemicals from petroleum wastewater is presently one of the most important aspects of pollution control in Oman.

Advanced oxidation processes (AOPs) have capability of rapid degradation of recalcitrant pollutants in the aquatic environment. Remediation of hazardous substances is attributed to hydroxyl radical (•OH), which exhibits reactivity toward organic. Many technical enhanced the production rate of •OH by chemical additives (such as H$_2$O$_2$), external energy (such as UV and sunlight), catalysts (such as TiO$_2$) and the
integration of two or more AOPs (such as TiO₂/Fenton/sunlight) [1].

Photo-catalysis is a promising technique for the treatment of contaminated water, which has been widely studied in recent years because it is fast, effective, eco-friendly, economically viable and able to completely oxidize organic molecules at a low energy cost [2].

Several previous studies have reported the enhanced oxidation of contaminants by photo-catalyst of TiO₂. It has been found that solar photo-catalytic oxidation process was effective in treating a synthetic high COD wastewater, it effectively reduced the COD content by 86% [3]. Javad Saien and Fatemeh Shahrezaei [8] showed that 78% of the COD was removed from real refinery wastewater, containing a range of aliphatic and aromatic organic compounds which were collected from the Kermanshah (Iran) refinery plant, by using the photo-catalyst in UV/TiO₂ process. Jose [4] reported that the use of solar photocatalysis in the presence of TiO₂ constituted a very effective and rapid method for the reduction and even elimination of these pesticides in leaching water. Ramanjot [5] showed that 83% of the Procion Blue (PB) dye was removed from industrial wastewater, containing a range of dyes which were collected from the collected from textile mill (Punjab), by using the photo-catalyst in sunlight/TiO₂ process. Santos [6] reported that photocatalysis (TiO₂/UV) achieved high rates of removal for phenols, oil and grease, and dissolved organic carbon from petroleum refinery wastewaters which were collected from the a Brazilian oil refinery plant. Shanmuga [7] carried out solar photo-catalytic experiments with 0.2 g/l of TiO₂ catalyst for different concentrations of phenol wastewater and it was found that complete degradation of phenol was possible in a reasonable time (less than 300 min) when concentration of phenol was ≤100 ppm.

This work evaluates the solar photo-catalyst of TiO₂ on the degradation of COD and TOC in petroleum wastewater. So, the main aims for this study are as follows:

- To evaluate the performance of employing the solar photo-catalyst of TiO₂ by a central composite design (CCD) with response surface methodology (RSM) to degradation of TOC and COD from the petroleum wastewater.
- To evaluate the statistical relationships among operating variables (such as TiO₂ dosage, pH, C₀ of COD, and reaction time) and the responses, which COD & TOC removal efficiencies are selected as the responses for optimization.
- To determine the optimum operational conditions of this method.

2. Materials and methods

2.1. Wastewater characterization

The physicochemical characteristics of the petroleum wastewater from Sohar oil refinery (SOR) are summarized in Table 1. The samples of raw effluent are collected in different days from the point that the wastewater is just leaving the dissolved air flotation (DAF) and just into the biological treatment unit in wastewater treatment plant at Sohar petroleum refinery. Samples are transferred to the laboratory and stored under refrigeration (4 °C) until use. Samples are characterized before the experiments to obtain their chemical and physical properties. Petroleum waste water characterization is determined by the quantification of pH, chemical oxygen demand (COD), and Total Organic Carbon (TOC) according to the Standard Methods for the Examination of Waste water methodology.

3. Materials

The catalyst is TiO₂ Aeroxide P-25 (manufactured by Evonik Industries Co in Germany). They are used for the solar photo-catalyst of TiO₂ process to degradation of TOC & COD. Sulfuric acid and sodium hydroxide are used to adjust the pH to the desired values.

| No | Parameter                  | Range of concentrations in petroleum wastewater | Average | The standard discharge limit |
|----|----------------------------|-----------------------------------------------|---------|------------------------------|
| 1  | pH                         | 6–8                                          | 7       | 6–9                          |
| 2  | Conductivity (Micro S/cm)  | 2600–3950                                    | 3275    | 2000–2700                    |
| 3  | TDS (ppm)                  | 1200–1500                                    | 1350    | 1500–2000                    |
| 4  | TOC (ppm)                  | 220–265                                      | 243     | 50–75                        |
| 5  | COD (ppm)                  | 550–1600                                     | 1075    | 150–200                      |
3.1. Analytical procedure and characterization of the industrial effluent

A Shimadzu TOC analyzer (LCSH/CSN) is used to measure the TOC for each sample. Chemical oxygen demand (COD) is measured by COD photometer (manufactured by CHEMetrics). COD is estimated before and after treatment. Before each analysis, samples are filtered by filter papers (0.22 μm Millipore Durapore membrane, 40 Ashless, Diameter 150 mm). Solar ultraviolet radiation (UV) is measured by a global UV radiometer (KIPP & ZONEN).

3.2. Experimental procedure

A sketch of the solar photo-catalyst of TiO₂ process is shown in Fig. 1. It consists of a glass recirculation tank (1.5 L), which is subjected to stirring to maintain a well-mixed solution during the experiments, connects to the tubular solar reactor (four tubes (50 cm length × 2 cm inner diameter × 0.1 cm thickness)). The solution is re-circulated through the reactor at a flow rate of about 1.5 L/min by means of a peristaltic pump. The catalyst materials are added in a glass recirculation tank during this process. The solar radiation intensity is approximately 650 W/m² during experimental runs. All experimental are carried out in same duration (12 P.M. – 3 P.M.). The tubular photo reactor operate at a UV-index from 8 to 11 according to Exposure category is very high.

The UV-Index is calculated as follow:

Take the output from the UV-E radiometer according to ISO 17166:1999/CIE S007/E-1998. Transform the output voltage to W/m² with the instruments sensitivity. Eq. (1) allows calculating the amount of UV intensity received on any surface in the same position with regard to the sun by UV-Index (UVI):

\[
\text{UVI} = \frac{R}{40} \text{W/m}^2
\]

(1)

Fig. 1. A sketch of the solar photo-catalyst of TiO₂ process.
where:

UVI is the UV-Index as shown in Fig. 2.
R is the reading (R) in UV radiometer by \((W/m^2)\) unit.

The pH for petroleum wastewater samples is used between 6 and 9. Several set of experiments are carried out according to a central composite design (CCD) with response surface methodology (RSM) to determine the COD and TOC removal efficiency under the optimum operational conditions.

4. Results and discussion

4.1. Experimental design and the analysis of variance (ANOVA)

Central composite design and response surface methodology are employed in the statistical design of the experiments, data analysis, explaining the optimal conditions of the independent variables and assessment of the relationships among four significant independent variables, which are TiO₂ dosage, pH, \(C_0\) of COD, and reaction time as shown in Table 2.

Each independent variable is varied over three levels according to face centered CCD as \(-1, 0, \) and \(+1\), respectively at the determined ranges base on a set of preliminary experiments. The total number of experiments conducts for the four factors according to Eq. (2)

\[
\text{No. of Experiments} = 2^k + 2k + 6
\]

(2)

where;

\(k\) is the number of factors.

Table 2

| The factors | Level of value |
|-------------|----------------|
|             | \(-1\) | 0   | \(+1\) |
| pH          | 6     | 7.5 | 9     |
| TiO₂ (g/l)  | 0.5   | 1   | 1.5   |
| COD (ppm)   | 850   | 1225| 1600  |
| RT \(^a\) (min) | 60   | 120 | 180   |

\(^a\) Reaction time.

Fig. 2. UV-index which measures UV intensity levels on a scale of 1–12.

The design consisted of \(2^k\) factorial points augmented by \(2k\) axial points and 6 replications for a center point. In this work, the total number of experiments conducted for the four factors is 30 with 16 factorial points, 8 axial points and 6 replications to assess the pure error and get a good estimate. The COD and TOC removal are the dependent variables (responses) during this process. Performance is evaluated by analyzing the COD and TOC removal efficiencies as shown in Table 3.

The behavior of the system is explained through an empirical second-order polynomial model, as shown in Eq. (3) [10].

\[
Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{j<k}^{k} \beta_{jj} X_j X_k + \epsilon_i
\]

(3)

where;

\(Y\) is the response.
\(X_i\) and \(X_j\) are the variables.
\(\beta\) is the regression coefficient.
\(k\) is the number of factors studied and optimize in the experiment.
\(\epsilon_i\) is the random error.

A total of 30 runs are executed using the Central Composite Design (CCD) experimental design; interactions among the four independent variables are considered in each run to investigate the validity of treating petroleum waste water using solar photocatalyst of TiO₂ during advanced oxidation. As shown in Table 3, the removal efficiencies range from 6.1% to 15.6% for TOC and 12% to 55.8% for COD.

The analysis of variance (ANOVA) is used for graphical analysis of data to obtain the interaction among the process variables and the responses. The quality of the fit polynomial model is expressed by coefficient of determination \((R^2)\). Model terms are evaluated by the \(P\)-value (probability) with 95% confidence level. The analysis of variance (ANOVA) for TOC and COD removal are represented in Table 4. All of the response surface quadratic models for parameters in this table are significant at the 5% confidence level since the \(P\)-values are less than 0.05. The
correlation coefficients ($R^2$) for the TOC and COD removal rates are 0.995, and 0.869, respectively, which they are greater than 0.80, the cut-off for a model with good fit. A high coefficient ($R^2$) value ensures a satisfactory adjustment of the quadratic model to the experimental data and illustrates good agreement between the calculated and observed results and shows that a desirable and reasonable agreement with the adjusted $R^2$ [9,11,12]. If the model terms have the P-value (probability) more than 0.05, they are considered limited influence. So, they must be excluded from the study to improve the models. Based on the results obtained, the response surface models for predicting TOC and COD removal efficiencies are considered reasonable.

4.2. Normal probability

In the current study, two quadratic models are significant model terms (Table 4). Insignificant model terms, which have limited influence, are excluded from the study to improve the models. Based on the results obtained, the response surface models for predicting TOC and COD removal efficiencies are considered reasonable.

The final regression models are presented in terms of their coded and actual factors (Table 5). Normal probability plots of the studentized residuals and diagnostics are provided by Design Expert 6.0.7 software program (a statistical software package from Stat-Ease Inc) to confirm that the selected models provide an adequate approximation of the real system. Plots of Normal probability aid in evaluating the models. Fig. 3 demonstrates the normal probability plots for the studentized residuals for TOC and COD removal efficiencies. The normal probability plots
predict that if the residuals follow a normal distribution, as shown in Fig. 3, then the points will fall along a straight line for each case. However, some scattering is expected even with normal data; thus, the data can be considered to be normally distributed in the responses of certain models.

4.3. Three-dimensional plots of the regression and Optimization process:

To assess the interactive relationships among the independent variables and the responses of certain models, 3D surface response plots are created by Design Expert 6.0.7 (Fig. 4). The maximum TOC and COD removal efficiencies are 15.48%, 48.42%, respectively. The TiO_2 and pH are the two main factors that improve the TOC and COD removal. The actual factors for removing these parameters include C_0 of COD and RT. The current work reveals that photocatalyst of TiO_2 in an AOP is more efficient in direct reaction with the petroleum wastewater treatment, achieving the highest removal rates for TOC and COD at alkaline conditions (pH = 8).

Optimization is performed to determine the optimum values of TOC and COD removal efficiencies using Design Expert 6.0.7. According to the optimization step, the desired goal for the operational conditions (C_0 of COD, reaction time and pH) is chosen as “within” the range, while (TiO_2 dosage) is chosen as “within” the minimum range to reduce the treatment cost. The responses (TOC and COD removal) are defined as “maximum” to achieve the highest performance. The program combines individual desirability into a single number and then searches to optimize this function basing on the response goal. Approximately 15.5% TOC and 48.5% COD removal rates are predicted by the models under optimized operational conditions (Table 6).

| Table 4 |
| --- |
| ANOVA results and adequacy of the quadratic models for TOC and COD removal efficiencies. |
| Source | Sum of squares | Degrees of freedom | Mean square | F-value | Prob > F |
| --- | --- | --- | --- | --- | --- |
| TOC Model | 201.6712 | 7 | 28.81017 | 712.4886 | <0.0001 |
| A | 6.600556 | 1 | 6.600556 | 163.2347 | <0.0001 |
| B | 13.69389 | 1 | 13.69389 | 338.6561 | <0.0001 |
| C | 20.05556 | 1 | 20.05556 | 495.983 | <0.0001 |
| D | 9.533898 | 1 | 9.533898 | 235.7774 | <0.0001 |
| B^2 | 40.02204 | 1 | 40.02204 | 989.7631 | <0.0001 |
| D^2 | 6.833732 | 1 | 6.833732 | 169.0419 | <0.0001 |
| AB | 3.900625 | 1 | 3.900625 | 96.46422 | <0.0001 |
| Residual | 0.889591 | 22 | 0.040436 | | |
| Lack of fit | 0.823258 | 17 | 0.048427 | | |
| Pure error | 0.066333 | 5 | 0.013267 | | |
| Cor total | 202.5608 | 29 | | | |
| COD Model | 4491.044 | 7 | 641.5777 | 20.89347 | <0.0001 |
| A | 220.5 | 1 | 220.5 | 7.18075 | 0.0137 |
| B | 171.125 | 1 | 171.125 | 5.572816 | 0.0275 |
| C | 153.125 | 1 | 153.125 | 4.986632 | 0.0360 |
| D | 351.125 | 1 | 351.125 | 11.43465 | 0.0027 |
| A^2 | 668.9032 | 1 | 668.9032 | 21.78334 | 0.0001 |
| D^2 | 259.8407 | 1 | 259.8407 | 8.461911 | 0.0081 |
| AB | 395.0156 | 1 | 395.0156 | 12.86398 | 0.0016 |
| Residual | 675.5561 | 22 | 30.7071 | | |
| Lack of fit | 583.4561 | 17 | 34.32095 | | |
| Pure error | 92.1 | 5 | 18.42 | | |
| Cor total | 5166.6 | 29 | | | |

| Table 5 |
| --- |
| Final equation in terms of coded and actual factors. |
| Final equation in terms of coded factors: |
| TOC removal (%) = 14.8 + 0.61A + 0.87B + 1.1C + 0.7D – 3.4B^2 – 1.4D^2 – 0.5AB |
| COD removal (%) = 49.3 – 3.5A + 3.1B + 2.9C + 4.4D – 13.9A^2 – 8.7D^2 + 4.9BD |
| Final equation in terms of actual factors: |
| TOC removal (%) = -91.5 + 6.15TiO_2 + 24 pH + 0.003COD + 0.11RT – 1.5(pH)^2 – 0.0004(RT)^2 – 0.6TiO_2pH |
| COD removal (%) = -18.3 + 104.5TiO_2 – 4.6 pH + 0.007COD + 0.2RT – 55.7(TiO_2)^2 – 0.002(RT)^2 + 0.05(pH)RT |
In general, the value of COD is considered more accurate than the value of TOC in checking efficiencies of treatment in wastewater because the value of COD measures the oxygen required to oxidize the organic compounds in wastewater while the value of TOC measures the amount of carbon in wastewater (including dissolved carbon dioxide and carbon compounds such as amine and aromatic compounds). So, this technique seems efficient in reducing the organic contaminants because the achieved removal efficiency of COD is approximately 574 ppm as shown in Fig. 5. In addition, some reasons might be the relatively high COD and TOC values, the nature of organic compounds, and the photo-catalytic process.

The desirability function is found to be 0.903 for these optimum conditions. An additional experiment is then performed to confirm these optimum results, revealing agreement with the predicted response values as shown in Table 6.

5. Conclusion

In the present study, the performance of employing solar photo-catalyst of TiO₂ in the AOP on degradation of TOC and COD from petroleum wastewater at Sohar Oil Refinery in Oman is investigated. A central composite design (CCD) with response surface methodology (RSM) is applied to evaluate the relationships among operating variables, such as TiO₂ dosage, C₀ of COD, pH, and reaction time, to identify the optimum operating conditions. Quadratic models for the following two responses prove to be significant with

![Fig. 3. Design expert plot, normal probability plot of the studentized residuals for (a) TOC removal and (b) COD removal.](image)

![Fig. 4. Response surface models for TOC & COD removal efficiencies for a given TiO₂ dosage (0.6 g/L), C₀ of COD (1600 ppm), pH (8), reaction time (139 min).](image)

| Maximum TOC and COD removal efficiencies for model response and verification experiments under optimum conditions [TiO₂ dosage (0.6 g/L), C₀ of COD (1600 ppm), pH (8) and reaction time (139 min)]. |
|---|---|---|
| Unit | Selected solution | Lab experiments |
| TOC removal | % 15.48 | 16.5 |
| COD removal | % 48.42 | 45 |
| Desirability | — | 0.903098 |
very low probabilities (<0.0001): chemical oxygen demand (COD) and Total Organic Carbon (TOC). The obtained optimum conditions include a TiO2 dosage (0.6 g/L), C0 of COD (1600 ppm), pH (8), reaction time (139 min). TOC and COD removal rates are 15.5% and 48.5%, respectively.

The predictions correspond well with experimental results (TOC and COD removal rates of 16.5%, and 45%, respectively). The solar photo-catalyst of TiO2 of high COD wastewater is a unique treatment process utilizing renewable solar energy and treating the wastewater with minimum chemical input.

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