

# Evaluating the TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> dosage, pH, C<sub>0</sub> 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<sub>2</sub> dosage and pH are the two main factors that improved the TOC and COD removal while C<sub>0</sub> of COD and reaction time are the actual factors. The optimum conditions are a TiO<sub>2</sub> dosage (0.6 g/L), C<sub>0</sub> 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<sub>2</sub> 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<sub>2</sub>; 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<sub>2</sub>O<sub>2</sub>), external energy (such as UV and sunlight), catalysts (such as TiO<sub>2</sub>) and the

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integration of two or more AOPs (such as  $\text{TiO}_2$ /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  $\text{TiO}_2$ . 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 Saïen 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/ $\text{TiO}_2$  process. Jose [4] reported that the use of solar photocatalysis in the presence of  $\text{TiO}_2$  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/ $\text{TiO}_2$  process. Santos [6] reported that photocatalysis ( $\text{TiO}_2$ /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  $\text{TiO}_2$  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  $\leq 100$  ppm.

This work evaluates the solar photo-catalyst of  $\text{TiO}_2$  on the degradation of COD and TOC in petroleum waste water. So, the main aims for this study are as follows:

- To evaluate the performance of employing the solar photo-catalyst of  $\text{TiO}_2$  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  $\text{TiO}_2$  dosage, pH,  $C_0$  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  $\text{TiO}_2$  Aeroxide P-25 (manufactured by Evonik Industries Co in Germany). They are used for the solar photo-catalyst of  $\text{TiO}_2$  process to degradation of TOC & COD. Sulfuric acid and sodium hydroxide are used to adjust the pH to the desired values.

Table 1  
Characteristics of petroleum wastewater from Sohar oil refinery (SOR).

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

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