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COMPARATIVE STUDY OF ADVANCED OXIDATION PROCESSES TO TREAT PETROLEUM WASTEWATER

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This study was carried out to compare the performance of different oxidation processes, such as solar photo-Fenton reaction, solar photocatalysis by TiO_2, and the combination of the two for the treatment of petroleum wastewater from Sohar Oil Refinery by a central composite design with response surface methodology. The degradation efficiency was evaluated in terms of chemical oxygen demand (COD) and total organic carbon (TOC) reductions. Solar photocatalysis by the TiO_2/Fenton method improved the performance of the photocatalyst at neutral pH for petroleum wastewater without the need to adjust the pH during this treatment. Under acidic conditions, the solar photo-Fenton process is more efficient than solar TiO_2 photocatalysis while it is less efficient under alkaline conditions. The TiO_2 dosage and pH are the two main factors that improved the TOC and COD reductions in the solar photocatalysis using combined TiO_2/Fenton and the solar TiO_2 photocatalysis processes while the pH and H_2O_2 concentration are the two key factors that affect the solar photo-Fenton process.

Keywords: solar photo-Fenton process, solar photocatalysis by TiO_2, petroleum wastewater, chemical oxygen demand, total organic carbon

1. Introduction

A major problem facing industrialised nations is contamination of the environment by hazardous chemicals. A wide range of pollutants have been detected in petroleum wastewater at Sohar Oil Refinery (SOR). Therefore, 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 the capability of rapid degradation of recalcitrant pollutants in aquatic environments. Remediation of hazardous substances is linked to the hydroxyl radical since it has the potential to degrade organic pollutants [1]. The advantages of AOPs are that these processes can occur at very low concentrations and do not form environmentally hazardous byproducts [2]. During the solar photocatalysis by TiO_2, upon exposure to sunlight an electron hole is created in the valence band of TiO_2 and concomitantly an electron is injected into the conduction band in response to light absorption. This electron hole causes the oxidation of hydroxyl anions and produces the hydroxyl radicals at the TiO_2 surface. During the photo-Fenton process the hydroxyl radicals are formed from the reaction of Fe^{2+} with H_2O_2 under sunlight irradiation. In the treatment of non-biodegradable and toxic compounds, the photocatalytic processes have shown promising results [3].

Previous studies have reported the enhanced oxidation of contaminants by TiO_2 photocatalysis in the presence of Fenton reactivity. Kim *et al*. [4] reported that the combination of TiO_2 photocatalysis and the Fenton-like reaction synergistically increased the degradation of organic compounds at around neutral pH (6.5–7.5) by the increased production of reactive oxidants and their improved reactivity. However, it has not been clearly addressed whether the integration of the UV/TiO_2 and Fe^{2+}/H_2O_2 systems exhibits synergistic results with respect to the degradation of contaminants. Little data are available on the role of Fe^{2+} ions in the UV/Fe^{2+}/TiO_2 system at neutral pH, where the Fe^{2+}/H_2O_2 or UV/Fe^{2+}/H_2O_2 system alone is not effective for oxidant production and pollutant oxidation due to the low aqueous iron solubility and H_2O_2 decomposition via a non-radical mechanism without hydroxyl radical generation [1,4,5]. Zarei *et al*. [6] showed that the removal efficiency of phenol was 69% after 150 min using photoelectro-Fenton (PEF)/Mn^{2+}/TiO_2 nanoparticles for the removal of phenol from aqueous solutions. Nogueira [7] showed that the role of Fe^{2+} ions and H_2O_2 are much more important than that of TiO_2 in the photodegradation of both 4-chloro-phenol (4CP) and dichloro-acetic acid (DCA) under solar irradiation [7].

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Table 1. Overview of research done in the area of Fenton/TiO_2 processes in recent years.

No.	Wastewater	method	material removed	Ref.
1	aqueous imidacloprid	photocatalysis by TiO_2 photo-Fenton	imidacloprid	[1]
2	Milli-Q water	TiO_2/Fenton-like/solar	2,4-dinitrophenyl hydrazine (DNPH)	[4]
3	aqueous solutions	TiO_2/photoelectro-Fenton/Mn^{2+}/UV	phenol	[6]
4	aqueous media	TiO_2/Fenton-like/solar	4-chloro-phenol (4CP) and dichloro-acetic acid (DCA)	[7]
5	oil-water emulsions	$TiO_2/H_2O_2/Fe^{2+}$/UV $TiO_2/H_2O_2/Fe^{2+}$/UV/air $ZnO/H_2O_2/Fe^{2+}$/UV	organics measured by reduction in COD value	[9]
6	dye polluted water	$TiO_2/H_2O_2/Fe^{2+}$/UV $TiO_2/H_2O_2/Fe^{2+}$/solar	azo dye basic blue 4	[11]
7	petroleum wastewater	$TiO_2/H_2O_2/Fe^{2+}$/solar solar photocatalysis by TiO_2 solar photo-Fenton	organics measured by reduction in COD and TOC values	This study

Table 2. Characteristics of petroleum wastewater from Sohar Oil Refinery (SOR).

parameters	units	ranges of concentration in petroleum wastewater	average concentration	standard discharge limit
pH	-	6–8	7	6–9
Conductivity	μS cm^{-1}	2600–3950	3275	2000–2700
TDS	ppm(mg dm^{-3})	1200–1500	1350	1500–2000
TOC	ppm (mg dm^{-3})	220–265	243	50–75
COD	ppm(mg dm^{-3})	550–1600	1075	150–200

The aims of the given study are as follows: (i) comparison of the homogenous (solar photo-Fenton) and heterogeneous photocatalytic systems (solar photocatalysis by TiO_2 and solar photocatalysis using combined TiO_2/Fenton processes) by central composite design (CCD) with response surface methodology (RSM) on the basis of their performances with regard to the chemical oxygen demand (COD) and total organic carbon (TOC) in petroleum wastewater and (ii) assessment of treatment efficiencies and the main factors with regard to these methods by CCD and RSM.

To our knowledge there are no reports in the literature of a similar comparison by a central composite design (CCD) with response surface methodology (RSM) applied to the homogeneous and heterogeneous photocatalytic systems for treatment of petroleum wastewater as shown in *Table 1*.

2. Materials and Methods

2.1. Wastewater Characterisation

The physicochemical characteristics of the petroleum wastewater from SOR are summarised in *Table 2*. Samples of the petroleum wastewater were collected on different days. Samples were transferred to the laboratory and stored in a refrigerator at 4 ºC until use. Samples were characterised before the analysis for their chemical and physical properties. The petroleum wastewater was characterised by the quantification of pH and chemical oxygen demand (COD) according to the Standard Methods for the Examination of Wastewater methodology [12].

2.2. Materials

The catalyst used was TiO_2 Aeroxide P-25 manufactured by Evonik Industries Co., Germany. Hydrogen peroxide (H_2O_2) (35% dm^3 dm^{-3}) and iron sulphate hydrate ($FeSO_4 \cdot xH_2O$) were supplied by EMPROVE Exp. (USA). Sulphuric acid and sodium hydroxide were used to set the desired pH values.

2.3. Analytical Procedures

A Shimadzu TOC analyser (LCSH/CSN) was used to measure the total organic content (TOC). Chemical oxygen demand (COD) was measured by a COD photometer (manufactured by CHEMetrics). The pH levels were monitored by using a digital pH meter. TOC and COD were determined before and after treatment. Before each analysis, samples were filtered by using a 0.22 μm Millipore Durapore membrane (40 ashless, diameter 150 mm) filter paper.

2.4. Experimental Procedure

The solar photocatalytic equipment used is shown schematically in *Fig.1* consisting of a stirred glass recirculation tank (1.5 dm^3). The tubular solar reactor contained four tubes 50 cm in length × 2 cm in inner diameter × 0.1 cm in thickness. The solution was recirculated through the reactor at a flow rate of 1.5 dm^3 min^{-1} using a peristaltic pump. Natural sunlight was used as a light source. The added materials and their concentrations such as TiO_2, H_2O_2, and Fe^{2+} were varied according to a central composite design (CCD) with response surface methodology (RSM) to determine the COD and TOC removal efficiencies under the optimum operational conditions.

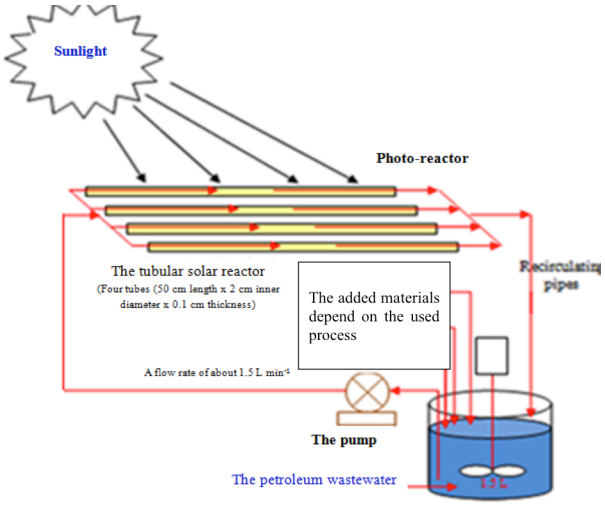

Figure 1. Schematic view of the experimental setup for solar photo-Fenton, solar TiO_2 photocatalysis and solar photocatalysis using combined TiO_2/Fenton processes.

3. Results and Analysis

3.1. Effect of pH

There are two types of Advanced Oxidation Processes (AOPs) depending on the reaction medium: a homogeneous process such as the solar photo-Fenton process, a heterogeneous process such as solar TiO_2 photocatalysis, and their combined processes. According to previous results [13], the solar photo-Fenton process is more efficient for petroleum wastewater treatment than solar TiO_2 photocatalysis under acidic conditions.

By comparing solar photocatalysis using combined TiO_2/Fenton processes with the solar photo-Fenton process under the same pH values, the TOC and COD removal efficiencies improved from 16% to 23% and from 27% to 38%, respectively at pH 7 as shown in *Table 3*. This enhancement is attributed to increased hydroxyl radical (•OH) production by the presence of TiO_2. As shown in *Fig.2*, solar photocatalysis using combined TiO_2/Fenton processes improves performance at neutral pH for petroleum wastewater. Therefore, there is no need to adjust the pH during this treatment.

By comparing these results with previous studies, the results of this work are in agreement with some studies. Ardhendu *et al*. [2] reported that the greatest TOC reduction took place under photo-Fenton process (PFP). It was found to be more efficient than UV/TiO_2 photocatalysis (UVPC) under acidic conditions. Gbandi *et al*. [3] found that photocatalysis of TiO_2 was independent of the pH of the solution, while under Fenton photocatalysis, the degradation rate of Orange II increases as the pH decreases. Duran *et al*. [8] found that the TiO_2 concentration and pH were the main factors for the TiO_2/Fenton/sunlight method for the degradation of the "blue 4" dye. Kim *et al*. [4] showed that the synergistic removal of benzoic acid by the UV/TiO_2/Fe^{3+}/H_2O_2 system was very efficient between

Table 3. Comparing the removal efficiencies (%) for three degradation processes expressed by TOC and COD under acidic pH range between 5.5 and 7 of petroleum wastewater.

Removal (%)	pH	TiO_2/ solar[a]	Fenton/ solar[b]	TiO_2/Fenton/ solar[c]
TOC	5.5	9	17	26
	7.0	15	16	23
COD	5.5	6	39	61
	7.0	24	27	38

experimental conditions: [a]1 g dm^{-3} TiO_2 and 180 min (RT); [b]1 g dm^{-3} H_2O_2, 0.04 g dm^{-3} Fe^{2+} and 180 min (RT); [c]1 g dm^{-3} TiO_2, 1 g dm^{-3} H_2O_2, 0.02 g dm^{-3} Fe^{2+} and 180 min (RT).

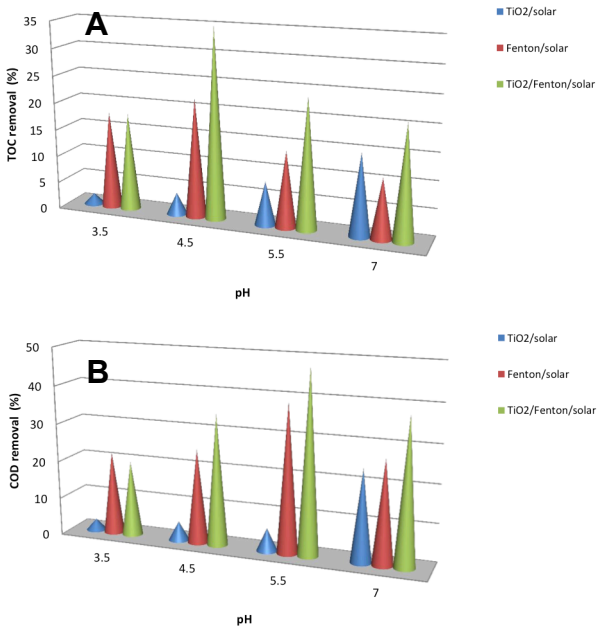

Figure 2. Comparison of the three degradation processess of TOC (A) and COD (B) under different pH values.

the pH values of 4 and 7. But, at higher pH values (pH>7), the addition of Fe^{3+} and H_2O_2 to the UV/TiO_2 system caused negative effects. However, Tony *et al*. [9] reported that the neutral pH of the oil-water solution was the optimum pH value for the degradation of COD by the Fenton/TiO_2/UV system.

3.2. Effect of Fenton Reagent and TiO_2 Concentration

The degradation of organic matter monitored by TOC and COD for solar TiO_2 photocatalysis is significantly improved by using a Fenton reagent in combination with solar photocatalysis as shown in *Fig.2* for the TiO_2/Fenton system. The excess iron has a negative effect because it reacts with hydroxyl radicals reducing the degradation rate of the pollutant [6]. Also, the excess amount of hydrogen peroxide can cause the auto decomposition of H_2O_2 to oxygen and water, and the recombination of hydroxyl radicals. Therefore, decreasing the concentration of hydroxyl radicals and

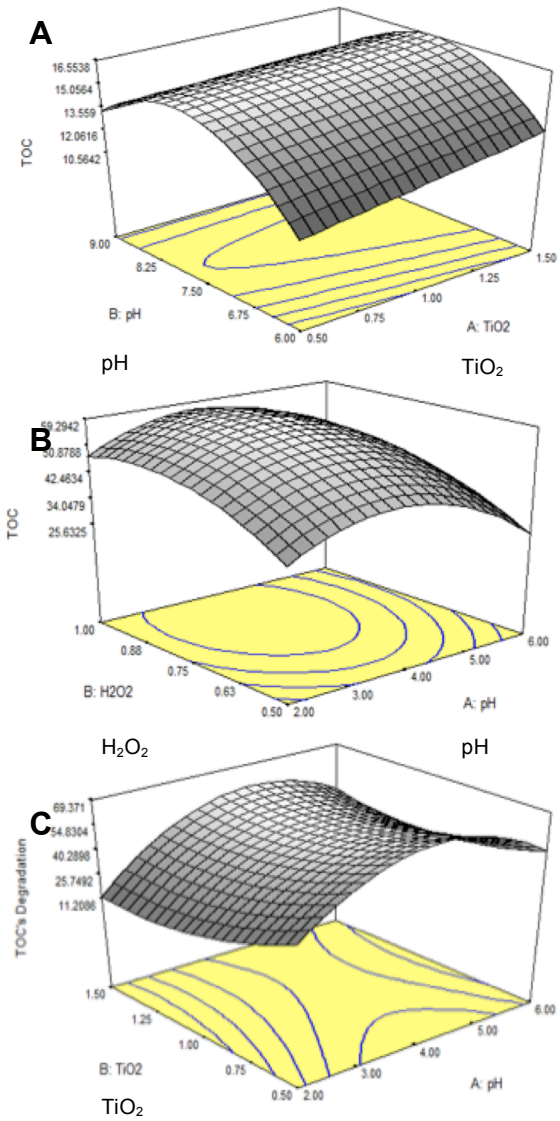

Figure 3. Response surface models for TOC pH val efficiencies for (A) solar photocatalysis by TiO_2 (B) solar photo-Fenton catalysis (C) solar photocatalysis by TiO_2/Fenton.

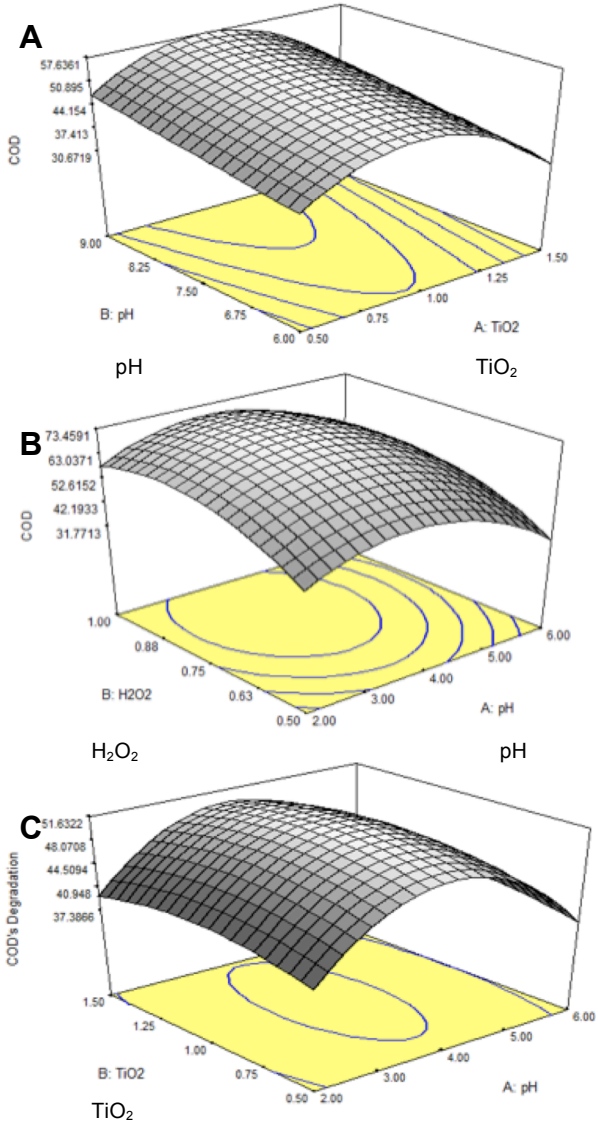

Figure 4. Response surface models for COD pH removal efficiencies for (A) solar photocatalysis by TiO_2 (B) solar photo-Fenton catalysis (C) solar photocatalysis by TiO_2/Fenton.

reagents reduces efficiency [9]. The degradation rate measured by COD and TOC increases as the TiO_2 concentration increases up to the optimum TiO_2 dosage in solar TiO_2 photocatalysis and solar photocatalysis using combined TiO_2/Fenton processes, which were 1 g dm^{-3} and 0.66 g dm^{-3}, respectively. However, TiO_2 dosages greater than the maximum value have a negative effect on these processes since the excess TiO_2 particles increase the turbidity of the solution that decreases the penetration of light into the solution resulting in a reduction in production of hydroxyl radicals (•OH) at the TiO_2 surface [10].

3.3. Treatment Efficiency

To assess the interactive relationships between the independent variables and the responses of certain models, 3D surface response plots were created by Design Expert 6.0.7. As shown in *Figs.3* and *4*, the TiO_2 dosage and pH were the two main factors that improved the TOC and COD values after removal under solar photocatalysis using the combined TiO_2/Fenton and solar TiO_2 photocatalysis processes, while the pH and H_2O_2 concentration were the two main factors in the solar photo-Fenton method. The greater removal rates from TOC and COD values under acidic conditions for solar photocatalysis using the combined TiO_2/Fenton and solar photo-Fenton methods were achieved with pH values of 3.6 and 4.2, respectively. However, they were under alkaline conditions (pH 8) for solar TiO_2 photocatalysis. The Fenton ratio and Fe^{2+} concentration were the essential variables for solar photocatalysis using the combined TiO_2/Fenton and solar photo-Fenton methods, respectively.

4. Conclusion

The given study evaluated the performance of advanced oxidation processes for the treatment of petroleum wastewater by a central composite design with response surface methodology. These processes include solar photo-Fenton catalysis, solar TiO_2 photocatalysis, and solar photocatalysis using the combined TiO_2/Fenton processes. The decomposition of organic matter was monitored by chemical oxygen demand and total organic carbon content. We obtained experimental evidence for the superior performance of solar photocatalysis using the combined TiO_2/Fenton methods over using TiO_2 only in the case of petroleum wastewater at neutral pH. Under acidic conditions, solar photo-Fenton process was found to be more efficient than solar TiO_2 photocatalysis. However, it was less efficient than the solar TiO_2 photocatalysis under alkaline conditions. The TiO_2 dosage and pH can be used to improve the TOC and COD values for solar photocatalysis using the combined TiO_2/Fenton processes and solar TiO_2 photocatalysis only. The pH and H_2O_2 concentration are the two main factors that influence the efficiency of the solar photo-Fenton process.

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