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Short Communication
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Comparative Study to the Solar Photo-Fenton, Solar Photocatalyst of TiO_2 and Solar Photocatalyst of TiO_2 Combined with Fenton Process to Treat Petroleum Wastewater by RSM

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Abstract

The present study is conducted to compare the performance of different oxidation processes such as the solar photo-Fenton, the solar photocatalyst of TiO_2 and solar photocatalyst of TiO_2/Fenton process for the treatment of petroleum wastewater from Sohar oil refinery (SOR) by a central composite design (CCD) with response surface methodology (RSM). The degradation efficiency is evaluated in terms of chemical oxygen demand (COD) and total organic carbon (TOC) reductions. The solar photocatalyst of TiO_2/Fenton method improved the performance of photocatalyst TiO_2 in the normal value of pH (7) for petroleum wastewater, therefore no need to adjust pH during this treatment. In acidic conditions pH <7, the solar photo-Fenton process is more efficient than the solar photocatalyst of TiO_2 process, while it is less efficient than the solar photocatalyst of TiO_2 process in alkaline conditions pH >7. The TiO_2 dosage and pH are the two main factors that improved the TOC and COD removal in the solar photocatalyst of TiO_2/Fenton and the solar photocatalyst of TiO_2 processes while the pH and H_2O_2 concentration are the two main factors in the solar photo-Fenton process.

Keywords: The solar photo-Fenton process; The solar photocatalyst of TiO_2 process; The solar photocatalyst of TiO_2/Fenton process; The petroleum wastewater; Chemical oxygen demand; Total organic carbon

Introduction

Recently, one of the major problems facing industrialized nations is contamination of the environment by hazardous chemicals. A wide range of pollutants 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. A hydroxyl radical has the potential to destroy and degrade organic pollutants [1]. Advantages of AOPs are that it occur even at very low concentration and don't form environmentally hazardous byproducts [2]. In the solar photocatalyst of TiO_2, when TiO_2 exposed to sunlight, a hole in the valence band and an electron in the conduction band are generated by light induction. This hole causes the oxidation of hydroxyl ions and produces the hydroxyl radicals at the TiO_2 surface. While in the photo-Fenton process, formation of hydroxyl radicals based on reaction between Fe^{+2} and H_2O_2 under sunlight irradiation. In treatment of non-biodegradable and toxic compounds, the photo-catalytic processes have shown promising results [3].

Several previous studies have reported the enhanced oxidation of contaminants by the photo-catalyst of TiO_2 system in the presence of Fenton. Kim [4] reported that the combination of TiO_2 photo-catalysis and the Fenton-like reaction synergistically increased degradation of organic compounds at circum-neutral pH (6.5-7.5) by increased production of reactive oxidants and improved the reactivity of the oxidant. However, it has not been clearly addressed whether the integration of the UV/ TiO_2 and Fe^{+3}/H_2O_2 systems exhibits synergistic results with respect to the degradation of the contaminant. Little data are available on the role of iron in the UV/TiO_2 system under neutral pH conditions, where the Fe^{+3}/H_2O_2 or UV/ Fe^{+3}/H_2O_2 system alone is not effective for oxidant production and pollutant oxidation due to the low aqueous iron solubility H_2O_2 decomposition via a non-radical mechanism (not leading to hydroxyl radicals generation) [1,4,5]. Zarei [6] showed that removal efficiency of phenol was 69.36% at 150 min using photo electro-Fenton (PEF)/Mn^{2+}/TiO_2 nano-particles for the removal of phenol from aqueous solutions. While Nogueira [7] showed that the roles of iron and H_2O_2 are much more important than that of TiO_2 in the photo degradation of both 4CP and DCA under solar irradiation [7].

The main aims for this study are the following:

- Comparison of the homogenous and the heterogeneous photo-catalytic systems (the solar photo Fenton, the solar photocatalyst of TiO_2 and solar photocatalyst of TiO_2/Fenton process) by "A central composite design (CCD) with response surface methodology (RSM)" based on their performance for the oxidation of chemical oxygen demand (COD) and total organic carbon (TOC) in petroleum wastewater.
- To assess treatment efficiencies and the main factors for these methods by "A central composite design (CCD) with response surface methodology (RSM)".

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

Materials and Methods

Wastewater characterization

The physicochemical characteristics of the petroleum wastewater from SOR are summarized in Table 2. Samples of the petroleum wastewater are collected in different days. Samples are transferred to the laboratory and stored under refrigeration (4ºC) until use. Samples are characterized before the experiments to obtain their chemical and physical properties. The petroleum wastewater characterization is determined by the quantification of pH, and chemical oxygen demand (COD) according to the standard methods for the examination of waste water methodology.

Materials

The catalyst is TiO_2 Aeroxide P-25 (manufactured by Evonik Industries Co in Germany). Samples of the petroleum waste water are collected from SOR. Hydrogen peroxide (H_2O_2) (35% (v/v)) and Iron sulfate hydrate ($FeO_{12}S_3$) are supplied by EMPROVE Exp (USA). Sulfuric acid and sodium hydroxide are used to adjust the pH to the desired values.

Analytical procedure

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). The pH levels are monitored by using a digital pH meter. TOC and COD are 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).

Experimental procedure

A sketch of the solar photocatalyst processes is shown in Figure 1. It consists of a glass recirculation tank (1.5 L), which is subjected to stirring, 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 sunlight is used as light source. The added materials and their concentrations such as TiO_2, H_2O_2 and Fe^{+2} depend on used process. The experiments for these processes 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.

Results and Discussion

Effect of pH

There are two types of advanced oxidation processes (AOPs) depended on type of reaction material; a homogenous process such as the solar photo-Fenton process and the heterogeneous process such as the solar photocatalyst of TiO_2 and the solar photocatalyst of TiO_2/ Fenton processes. According to the results, the solar photo-Fenton process is more efficient for petroleum wastewater treatment than the solar photocatalyst of TiO_2 process in acidic conditions pH <7.

By comparing the solar photocatalyst of TiO_2/Fenton process with the solar photo-Fenton process under the same pH values, the TOC and COD removals are improved from 16% to 23.2% and from 27% to 38%, respectively at pH 7 as shown in Table 3. This enhancement is attributed to increasing of the hydroxyl radicals (•OH) production by the presence of TiO_2. As shown in Figure 2, the solar photocatalyst of TiO_2/Fenton improves performance the solar photocatalyst TiO_2 and the solar photo-Fenton in the normal value of pH (7) for petroleum wastewater, therefore no need to adjust pH during this treatment.

No.	wastewater	method	Removal material	References
1	Aqueous imidacloprid	• Photocatalysis of 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/photo-electro-Fenton/Mn+2/UV	Phenol	[6]
4	Aqueous medium	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	COD	[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 41	[11]
7	Petroleum wastewater	• $TiO_2/H_2O_2/$ Fe^{+2} /solar • Solar photocatalyst of TiO_2 • Solar photo-Fenton	COD and TOC	This study

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

No	Parameter	Unit	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(mg/L)	1200-1500	1350	1500-2000
4	TOC	ppm (mg/l)	220-265	243	50-75
5	COD	ppm(mg/L)	550-1600	1075	150-200

Table 2: Characteristics of the petroleum wastewater from Sohar oil refinery (SOR).

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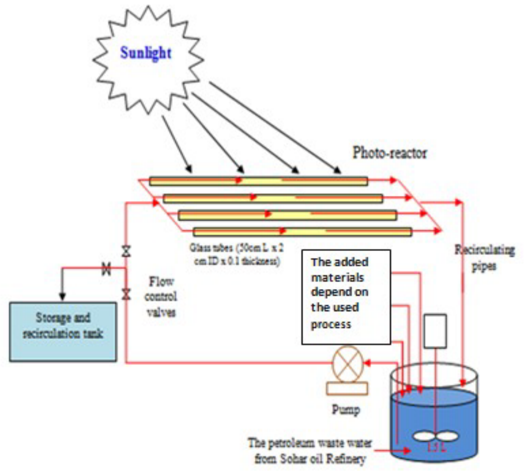

Figure 1: A sketch of the set up for the solar photo-Fenton, solar photocatalyst of TiO_2 and solar photocatalyst of TiO_2/Fenton process.

The removal (%)	pH	The process		
		TiO_2/solar*	Fenton/solar**	TiO_2/Fenton/solar***
TOC	5.5	9	17	25.7
	7	15	16	23.2
COD	5.5	6	39	61
	7	24	27	38

*Experimental conditions; 1 g/L TiO_2 and 180 min (RT). ** Experimental conditions; 1 g/L H_2O_2, 0.04 g/L Fe^{+2} and 180 min (RT). *** Experimental conditions; 1 g/L TiO_2, 1 g/L H_2O_2, 0.02 g/L Fe^{+2} and 180 min (RT).

Table 3: Comparing the three processes for degradation of TOC and COD under pH values ranges of petroleum wastewater (5.5-7).

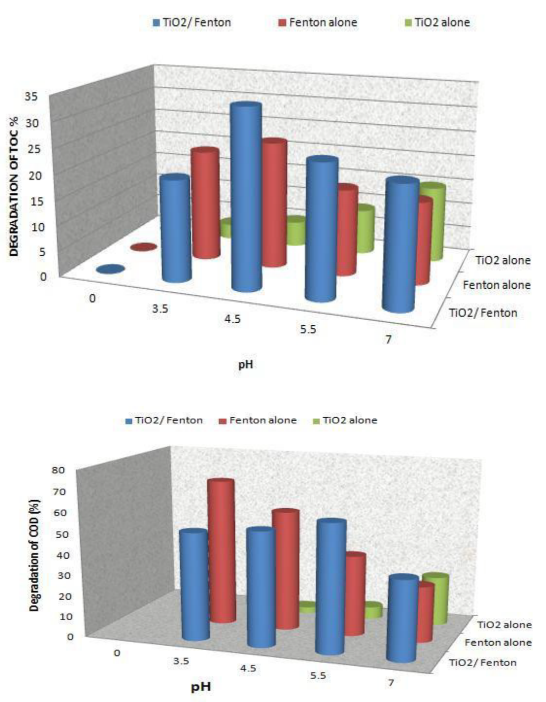

Figure 2: Comparing the three applications for degradation of TOC and COD under different pH values.

By comparing these results with previous studies, the results of this work are agreement with some studies. Ardhendu [2] reported that the highest TOC removal took place in photo-Fenton (PFP) and it is more efficient than the UV/ TiO_2 photocatalysis (UVPC) in acidic conditions. Gbandi [3] found that photocatalysis of TiO_2 was independent of the pH of the solution while, in Fenton, degradation rate of Orange II increases when 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 at the pH values ranging from 4 to 7. But, at higher pH values (pH>7), the addition of Fe^{+3} and H_2O_2 to the UV/TiO_2 system caused the negative effects. However, Tony et al., [9] has reported that the natural pH of the oil-water solution was the optimum pH value for degradation of COD by the Fenton/ TiO_2/UV system.

Effect of fenton reagent and TiO_2 concentration

The degradation of TOC and COD for the solar photocatalyst of TiO_2 are improved clearly by using Fenton reagent with it in the solar photocatalyst of TiO_2/Fenton system as shown in Figure 2. The excess iron has negative effect because it reacts with hydroxyl radicals and reducing degradation rate of 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. Thereby decreasing the concentration of hydroxyl radicals and reducing compound elimination efficiency [9]. The degradation rate of COD and TOC increases when the TiO_2 concentration increases until the optimum TiO_2 dosage in the solar photocatalyst of TiO_2 and solar photocatalyst of TiO_2/Fenton process which they are l g/L and 0.66 g/L, respectively. But the TiO_2 dosages after the maximum value have a negative effect in these processes. Where the excess TiO_2 particles increase turbidity of solution and cause decreasing the penetration of light into the solution resulting in a reduction in production of the hydroxyl radicals (•OH) at the TiO_2 surface [10].

Treatment efficiency

To assess the interactive relationships between the independent variables and the responses of certain models, 3D surface response plots are created by Design Expert 6.0.7. As shown in Figures 3 and 4, the TiO_2 dosage and pH are the two main factors that improved the TOC and COD removal in the solar photocatalyst of TiO_2/Fenton and the solar photocatalyst of TiO_2 methods while the pH and H_2O_2 concentration are the two main factors in the solar photo-Fenton method. The highest removal rates for TOC and COD at acidic conditions for the solar photocatalyst of TiO_2/Fenton and the solar photo-Fenton methods, which pH values are 3.68 and 4.2, respectively. However, they are at alkaline conditions (pH 8) for the solar photocatalyst of TiO_2 process. Fenton ratio and Fe^{+2} concentration are the actual factors for the solar photocatalyst of TiO_2/Fenton and the solar photo-Fenton methods, respectively. While initial concentration of COD is actual factor for the solar photocatalyst of TiO_2 [11].

Conclusions

In the present study, different oxidation processes such as the solar photo-Fenton, the solar photocatalyst of TiO_2, and solar photocatalyst of TiO_2/Fenton processes are conducted to compare their performances in the treatment of petroleum wastewater by a central composite design (CCD) with response surface methodology (RSM). The degradation efficiency is evaluated in terms of chemical oxygen demand (COD) and

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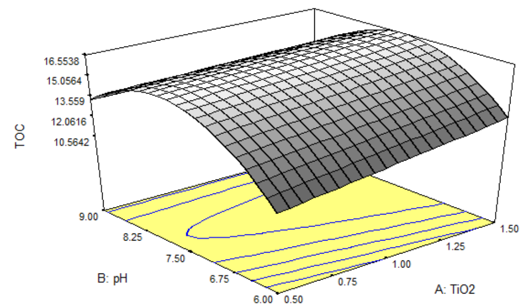
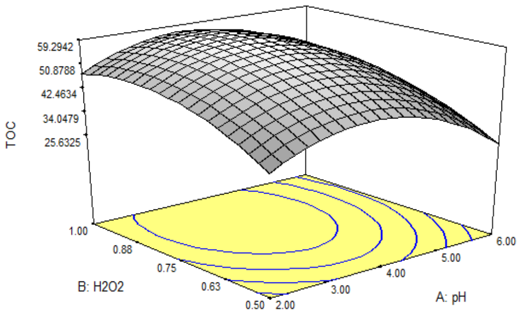
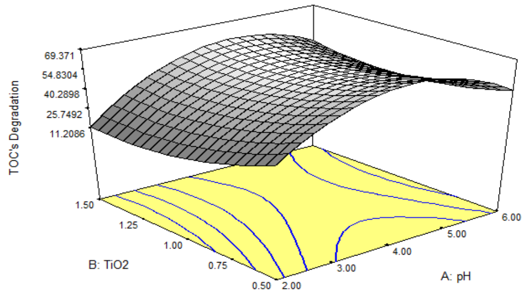


(a) ThesolarphotocatalystofTi02

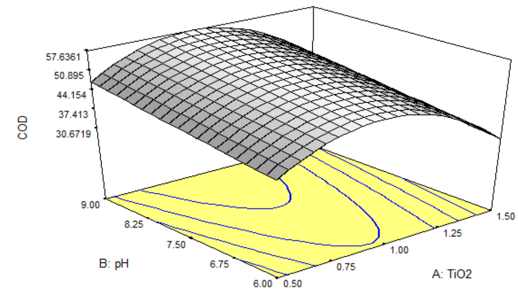


(b) The solar photo-Fenton

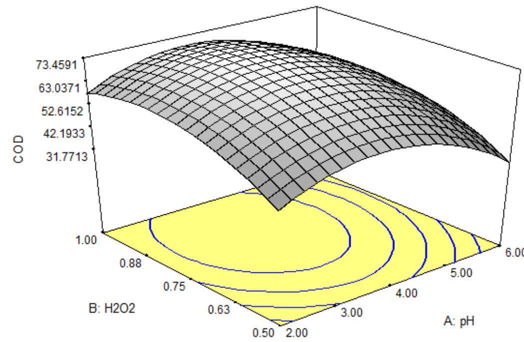


(c) Thesolarphotocatalystof Ti02/Fenton

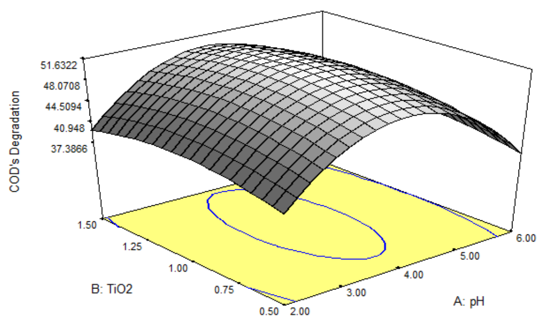
Figure 3: Response surface models for TOC removal efficiency.



(a) ThesolarphotocatalystofTi02



(b) The solar photo-Fenton



(c) Thesolarphotocatalystof Ti02/Fenton

Figure 4: Response surface models for COD removal efficiency.

total organic carbon (TOC) reductions. The solar photocatalyst of TiO_2/Fenton method improved the performance of photocatalyst TiO_2 in the normal value of pH (7) for petroleum wastewater, therefore no need to adjust pH during this treatment. In acidic conditions pH<7, the solar photo-Fenton process is more efficient than the solar photocatalyst of TiO_2 process, while it is less efficient than the solar photocatalyst of TiO_2 process in alkaline conditions pH>7. The TiO_2 dosage and pH are the two main factors that improved the TOC and COD removal in the solar photocatalyst of TiO_2/Fenton and the solar photocatalyst of TiO_2 processes while the pH and H_2O_2 concentration are the two main factors in the solar photo-Fenton process.

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