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Degradation of Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) in petroleum wastewater by solar Photo-Fenton process

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Abstract

The aim of this study is to investigate the performance of solar photo-Fenton process (H_2O_2/Fe^{2+}/Solar) to treat petroleum wastewater from Sohar oil Refinery, Oman. The effect of operating conditions such as pH, reaction time, Fenton ratio, and Fenton reagent concentrations are investigated. The obtained optimum conditions include H_2O_2 dosage (1 g L^{-1}), Fe^{+2} dosage (0.08 g L^{-1}), pH (3) and reaction time (180 min). TOC and COD removal rates are 64 % and 78 %, respectively. However, the photolytic process was less efficient in the petroleum wastewater treatment, achieving an 11.5% and 9% of COD and TOC removals, respectively. The solar photo-Fenton process has well efficient for petroleum wastewater treatment in the acidic conditions and more economic by free energy.

Keywords: Solar Photo-Fenton; Petroleum wastewater; Chemical oxygen demand (COD); Total Organic Carbon (TOC).

1. Introduction

Large amounts of water are used in the petroleum refinery activity and, consequently, significant volumes of petroleum wastewater are generated. Recently, 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 wastewater 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, which exhibits reactivity toward organic. AOPs may be used in petroleum wastewater treatment for overall organic content reduction (COD), specific pollutant destruction, sludge treatment, increasing bioavailability of recalcitrant organics and color and odor reduction (Tony *et al.*, 2012). One of the most important advanced oxidation processes (AOPs) is photo-Fenton process. There are two Fenton's reaction categories: the standard Fenton reaction between hydrogen peroxide and Fe^{+2} ions in solution, and the Fenton-like reaction where hydrogen peroxide reacts with Fe^{+3} or immobilized oxides (Yeh *et al.*, 2008). In the presence of light, Fenton's reaction promotes the so-called photo-Fenton process and a higher quantity of ·OH is produced. This is achieved using low-energy photons in the visible light spectrum, such as those generated by sunlight, making this technique economically viable (Torrades *et al.*, 2004). In comparison with other AOPs, the photo-Fenton's reaction presents some advantages, for example (Kositzia *et al.*, 2004) showed the solar photo-Fenton process appears to be more efficient for synthetic municipal wastewater in comparison to the TiO_2/oxidant system. These advantages because H_2O_2 slowly decomposed into oxygen and water. In addition, the abundance, lack of toxicity and ease of removal from water makes Fe^{2+} the most commonly used transition metal for Fenton's reaction applications (Badawy and Ali, 2006). Moreover, the generation of harmful by-products associated with Fenton's reaction applications is noticeably lower compared to some other AOPs (Morais and Zamora, 2005). The analysis of published papers on this field shows a large variation on reagents consumption and the amount of oxidable substances present in the waste water is a fundamental factor, which determines the necessary supply of reagents. However, an appropriate design of the photo-Fenton reactor and the utilization of a more efficient radiation system would contribute to improve process performance and, consequently, reduce reagents consumption. A number of studies have been conducted, showing that the combination of iron and hydrogen peroxide in the presence of light called photo-Fenton's reaction is an effective oxidant for a wide variety of organic substrates. Coelho *et al.*, (2006) reported that the photo-Fenton process was able to improve the DOC removal in a short period of time from Sourwater which was a specific stream of petroleum refineries and the maximum DOC removal attained was 87%. Previous work by Tony *et al.,*

(2012) used the photo-Fenton method for the oil-refinery wastewater achieved approximately 50% COD removal and the photo-Fenton parametric concentrations to maximize COD removal were optimized: pH=3, H_2O_2= 400 mg/L, and Fe^{2+}=40 mg/L. Rossiter *et al.,* (2013) showed that polycyclic aromatic hydrocarbons and aromaticity removal of approximately 92.7 and 96.2%, respectively, from petroleum-extraction wastewater were obtained by a photo-Fenton like process after 7 h of sunlight exposure and photo-Fenton process using sunlight achieved 53% COD removal.

The main aims for this study are as follows:

- To investigate the performance of solar photo-Fenton in petroleum wastewater treatment.
- To determine the optimum operational conditions of the proposed method.
- To compare the proposed method with the previous works.

2. Materials and methods

2.1. Wastewater Characterization

The physicochemical characteristic of the petroleum wastewater from SOR are summarized in Table 1. Samples of the petroleum wastewater were collected on different days. Samples were transferred to the laboratory and stored under refrigeration (4 °C) until use. Samples were characterized before the experiments to obtain their chemical and physical properties. The petroleum wastewater characterization was determined by the pH, COD, and TOC, which were quite high. This type of petroleum wastewater can be categorized as very dangerous on the environment and it excesses of the standard discharge limits for COD and TOC due to the presence of high organic substances.

Table 1. Characteristics of the petroleum wastewater from SOR

No	Parameter	Range of concentrations in petroleum wastewater	Average	The standard discharge limit*
1	pH	6-8	7	6 < pH > 9
2	Conductivity (Micro S/cm)	2600-3950	3275	< 2700
3	TDS (ppm)	1200-1500	1350	< 2000
4	TOC(ppm)	220 - 265	243	< 75
5	COD(ppm)	550-1600	1075	< 200
6	D.O. (ppm)	0.6-2.9	1.75	> 5
7	Phenol (ppm)	70-90	80	0.001
	Oil (ppm)	15-22	19	0.001
8	Iron (ppm)	<0.01	<0.01	2
9	Sulfite(ppm)	12-15	13.5	1.0

*Wastewater discharge standard of Oman (2005)

2.2. Materials

Samples of the petroleum wastewater are collected from Sohar oil refinery, Oman. Hydrogen peroxide (H_2O_2) (35% (v/v)) and ferrous sulfate are supplied by EMPROVE Exp (USA). Sulfuric acid (95-97%) and sodium hydroxide (50%) are used to adjust the pH to the desired values.

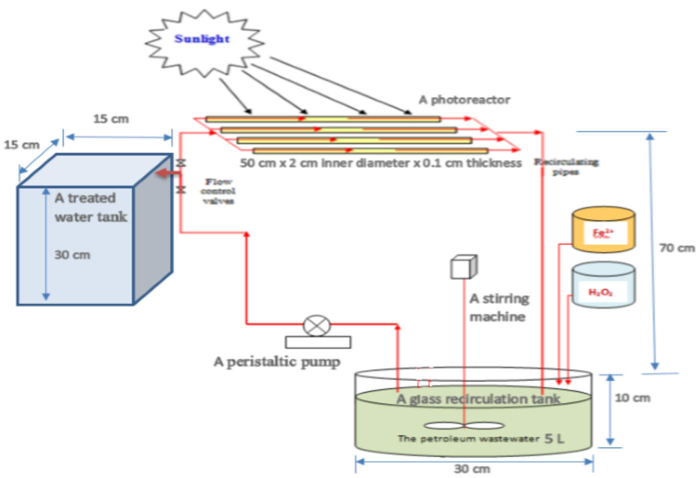

Figure 1. A sketch of the solar photo-Fenton process

2.3. Experimental procedure

A schematic design of the solar photo-Fenton process is shown in Figure 1. It consisted of a glass recirculation tank (7 L), which was subjected to stirring to maintain a well-mixed solution during the experiments, connected with the tubular solar reactor (9 tubes (50 cm length x 2 cm inner diameter x 0.1 cm thickness)) in order to increase the surface area exposed to sunlight according to preliminary study and literature (Senthilkumar and Aljoubory, 2014). The solution was re-circulated through the reactor at a flow rate of about 1.5 L/min (according to preliminary study) by means of a peristaltic pump (model; PEROCOM N-M PR2003). The chemical materials were added in a glass recirculation tank in this process. The pH of petroleum wastewater samples was used between 2 and 9 according to preliminary study and literature (Chu *et al.*, 2012). The photoreactor operated under exposure category of very high (8-11) according to a UV-index by a global UV radiometer (KIPP & ZONEN).

Several sets of experiments were carried out to evaluate the effectiveness of this process to treat the petroleum wastewater and investigate the influence of important operating parameters, including Fenton ratio, Fenton reagents dosages, pH and reaction time on removal efficiencies of TOC and COD from this type of wastewater.

2.4. Analyses

The Chemical Oxygen Demand (COD) for the petroleum waste water samples is measured by using a COD Photometer (manufactured by CHEMetrics) and their Total Organic Carbon (TOC) by using a TOC Analyzer (manufactured by SHIMADZU (TOC-LCSH/CSN)). In addition, the pH of the samples is measured by using a Water portable meter (model PCD650, EUTECH). Before each analysis, samples are filtered by filter papers (0.22 µm Millipore Durapore membrane, 40 Ashless, Diameter 150 mm) to remove precipitated iron-containing species. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (model: KIPP & ZONEN, ISO 17166:1999/CIE S007/E-1998). The UV-Index is calculated as follow:

The output voltage (v m^{-1}) from the UV-E radiometer transform it to W m^{-2} according to instructions of this radiometer model. The Equations (1 & 2) allows calculating the amount of UV intensity received on any surface in the same position with regard to the sun by UV-Index (UVI) as shown in Figure 2.

$$R(W/m^2) = 0.168\ R(v/m) \quad (1)$$

$$UVI = R\ (W/m^2)*40\ (m^2/W) \quad (2)$$

Where:

-UVI is the UV-Index.

-R is the reading (R) in UV radiometer by (W/m^2) unit.

1	2	3	4	5	6	7	8	9	10	11	12
Low		Moderate			High		Very high				Extreme

Figure 2. UV-Index which measures UV intensity levels on a scale of 1 to 12

3. Results and discussion

3.1. Effect of H_2O_2 to Fe^{2+} ratio

Several Fenton ratios (H_2O_2/Fe^{2+}), which were 5, 9, 12.5, 25, 50, 75, and 100, were tested to investigate the optimum value. These experiments were done with optimal pH 3 as shown in Figure 3. The results showed that the optimal ratio of H_2O_2/Fe^{2+} was 12.5, and the maximum removal rates of TOC and COD were 64% and 78%, respectively as shown in Figure 3. The oxidation process led to an increase in the concentration of hydroxyl radicals up to a certain concentration when the hydrogen peroxide ratio increased (Rahman and Al-Malack, 2006). When hydrogen peroxide increased more, it started to react with hydroxyl radicals, acting as a free-radical scavenger (Zazouli *et al.,* 2012).

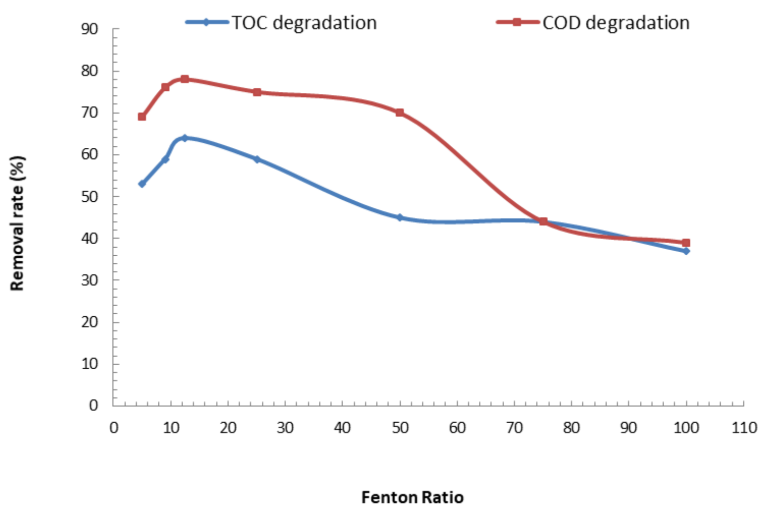

Figure 3. Effect of the H_2O_2/Fe^{2+} ratio on the degradation rate of TOC and COD by the solar photo-Fenton process in petroleum waste water (pH = 3; 180 min)

3.2. Effect of H_2O_2 dosage

The dosing rate of hydrogen peroxide (H_2O_2) is considered to be one of the most important factors, which should be considered in the solar photo-Fenton process. To determine the optimal H_2O_2 dosage to treat the petroleum wastewater by using solar photo-Fenton process and the effect H_2O_2 concentration on COD and TOC removals, the H_2O_2 dosages were changed from 1 to 8 g L^{-1} while keeping the concentration of Fe^{+2} dosage at 0.08 g L^{-1}. The results obtained from experiments with varying H_2O_2 dosages from 1 to 8 g L^{-1} at pH 3 and 180 min were illustrated in Figure 4.

The results showed the variation of degradation. The degradation of COD and TOC increased with H_2O_2 dosages up to about 1 g L^{-1}, while it decreased above this dosage. Thus, the H_2O_2 dosage of 1 g L^{-1} was considered the optimal H_2O_2 dosage at pH 3 and 180 min. However, when the concentration of H_2O_2 exceeded the optimal value, the reaction rates decreased as a result of the so-called scavenging effect of an excess of H_2O_2 reacting with hydroxyl radical ($^{\cdot}OH$) (Chu, 2001). The excess of H_2O_2 reacted with the hydroxyl radical ($HO^{\cdot}$) resulting in the radical hydroperoxyl ($HO^{\cdot}_2$) (E^0 = 1.8 V), which has lower oxidation potential than the hydroxyl radical (E^0 = 2.8 V) (Equation (3)) (Chu and Wong 2004; da Silva *et al,*. 2015; Dionysiou *et al.,* 2000) and might be attributed to the autodecomposition of H_2O_2 to Oxygen (O_2) and water (H_2O) (Equation (4)). Moreover, the recombination of hydroxyl radical ($^{\cdot}OH$) and the radical hydroperoxyl ($HO^{\cdot}_2$) was increased as shown in Equation (5) (Neyens and Baeyens, 2003);

$$H_2O_2 + HO^{\cdot} \rightarrow HO^{\cdot}_2 + H_2O \quad (3)$$

$$H_2O_2 \rightarrow \frac{1}{2} O_2 + H_2O \quad (4)$$

$$HO^{\cdot} + HO^{\cdot}_2 \rightarrow + H_2O + O_2 \quad (5)$$

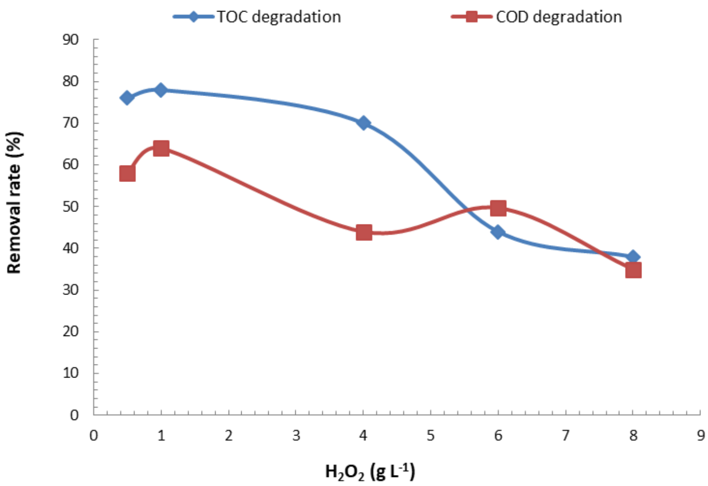

Figure 4. Effect of the H_2O_2 dosage on the TOC and COD removals by the solar photo-Fenton processes (pH 3; 0.08 g L^{-1} Fe^{+2}; 180 min)

3.3. Effect of Fe^{2+} dosage

The amount of ferrous iron (Fe^{+2}) is one of the main parameters, which influence the photo-Fenton processes. To determine the optimal Fe^{+2} dosage to treat the petroleum wastewater by using solar photo-Fenton process and the effect of Fe^{+2} concentration on COD and TOC removals, the Fe^{+2} dosages were changed among 0.04, 0.08, 0.11 and 0.20 g L^{-1} while keeping the H_2O_2 dosage at 1 g L^{-1}.

The results obtained from experiments with varying Fe^{+2} dosages among 0.04, 0.08, 0.11 and 0.20 g L^{-1} at pH 3 and 180 min were illustrated in Figure 5. The results showed the variation of degradation. The degradation of COD and TOC increased with Fe^{+2} dosages up to about 0.08 g L^{-1} while it decreased above this value of dosage. Thus, the Fe^{+2} dosage of 0.08 g L^{-1} was considered the optimal Fe^{+2} dosage at pH 3 and 180 min. However, the extended Fe^{+2} concentrations above 0.08 g/L could not extend COD and TOC removal efficiency due to the excess iron reacted with hydroxyl radicals producing compounds, which inhibited the reaction rates (Equation (6)) (Tony *et al.,* 2009). In addition, the increase of a brown turbidity in the wastewater during the solar photo-Fenton treatment hindered the absorption of the sunlight light required during the photo-Fenton process (Rodrigues *et al.,* 2009).

$$Fe^{+2} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^{-} \quad (6)$$

It is worth noting that, in the photo-Fenton process, the amounts of Fe^{2+} ions should be as low as possible for economic and environmental reasons (Ramirez *et al.,* 2007).

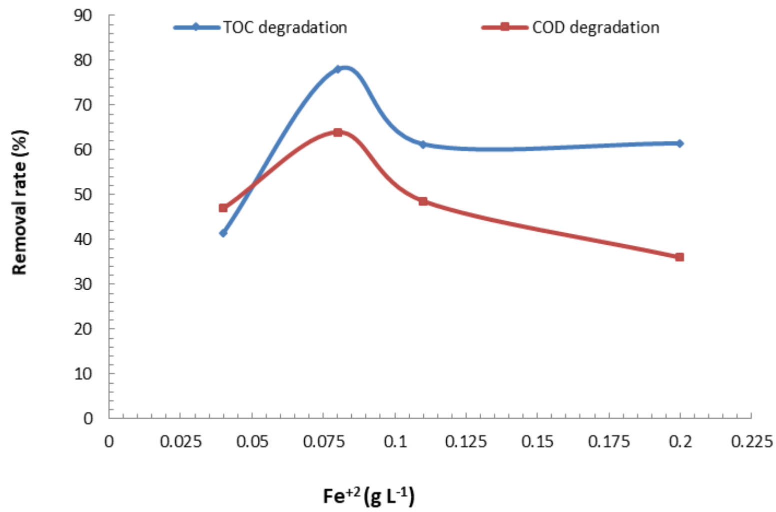

Figure 5. Effect of the ferrous iron (Fe^{+2}) dosage on the TOC and COD removals by the solar photo-Fenton processes (pH 3; 1 g L^{-1} H_2O_2; 180 min)

3.4. Effect of pH

The pH value influences the generation of hydroxyl radicals and the oxidation efficiency. The pH significantly affect the solar photo-Fenton process because it influences the activity of both the speciation of iron and hydrogen peroxide decomposition.

The experiments were carried out at a pH within the range of 2-8. As shown in Figure 6, the results showed that the optimal pH was 3 at 180 min. The degradation of TOC and COD decreased after pH 3 because the oxidation potential of the hydroxyl radical ($^{\cdot}OH$) decreased with increasing pH (Lucas and Peres, 2009) and the iron species such as $Fe^{3+}(OH)_2$, which were less photoactive, predominated (Rubio-Clemente *et al.,* 2015). Another reason was the dissociation and autodecomposition of H_2O_2 (Badawy and Ali, 2006). In addition, The pH higher than 3 led to a decrease in the level of free iron ions because of the formation of ferric hydroxides ($Fe(OH)_3$), which precipitated (Batista and Nogueira, 2012; Pignatello *et al.,* 2006).

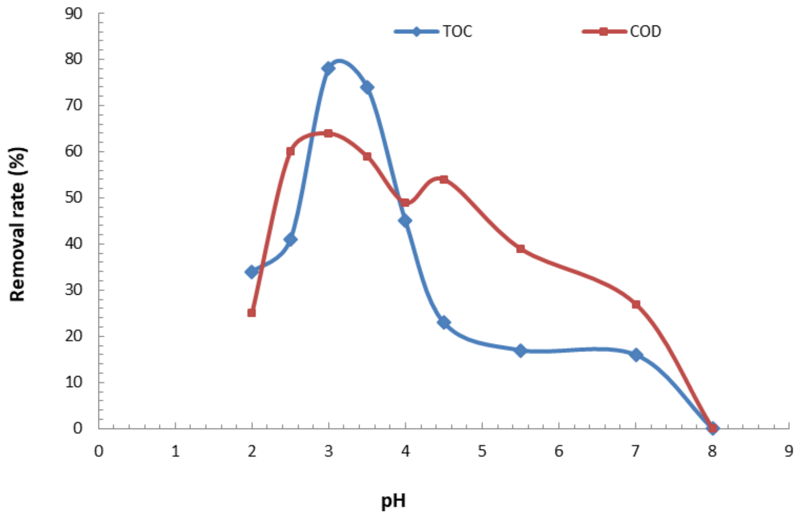

Figure 6. Influence of the initial pH on the degradation rate of TOC and COD by the solar photo-Fenton process

For pH values below 3, the reaction of hydrogen peroxide with Fe^{2+} was seriously affected causing a reduction in hydroxyl radical production due to hydroxyl-radical scavenging by H^+ ions (Lucas and Peres, 2009). In addition, the activity of the Fenton reagent was reduced in an extremely acidic medium (pH < 3). This could be due to the generation of stable oxonium ions ($H_3O_2^+$) through the solvation of a proton by H_2O_2 (Babuponnusami and Muthukumar, 2014; Sun *et al.,* 2008). These observations were in accordance with those reported by Paterlini and Nogueira, (2005) and Kang and Hwang, (2000) who found that an acidic pH (2.5-4) was optimum for the photo-Fenton process

3.5. Effect of reaction time

The degradation rate of TOC and COD by the solar photo-Fenton process to treat the petroleum wastewater was monitored continuously during the reaction. As shown in

Figure 7, the reaction rate increased with increasing reaction time but after about 120 min, it diminished.

These findings might be explained by the production of hydroxyl radicals increased until 120 min as shown in Figure 7. Thereafter, the reaction rate diminished as the hydrogen peroxide was consumed, which was the primary source for the generation of the hydroxyl radicals (Tony *et al.,* 2012). In addition, the photo-Fenton reaction needs longer irradiation time since the petroleum wastewater commonly contains high molecular weight and complex structured organic pollutants (da Silva *et al.,* 2015).

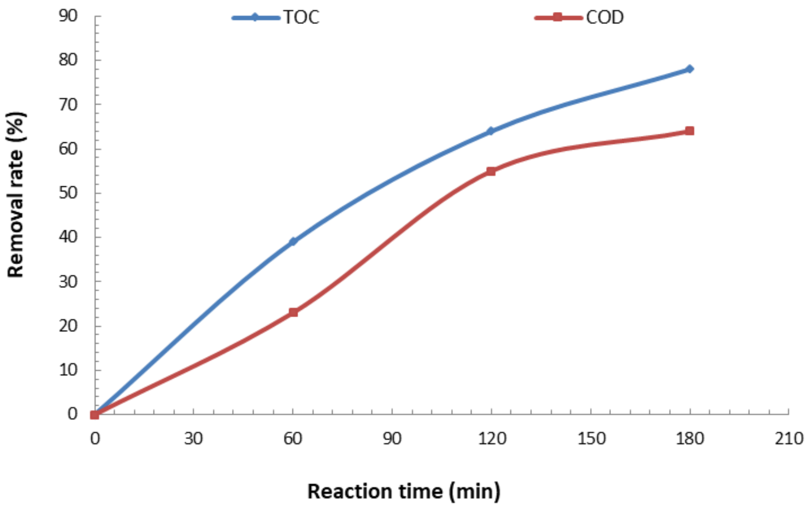

Figure 7. Influence of the reaction time on the degradation rate of TOC and COD by the solar photo-Fenton process

Table 2. Overview of work done in the photo-Fenton application in recent years

No.	The process	Wastewater type	Removed material	Max. Removal efficiency (%)	Ref.
1	H_2O_2/Fe^{2+}/Solar	petroleum-extraction wastewater	COD	53%	(da Rocha *et al.* 2013)
2	H_2O_2/ Fe^{+2}/UV	oil-water emulsion	COD	50%	Tony *et al.* (2012)
3	H_2O_2/Fe^{2+}	Semi-aerobic landfill leachate.	COD	58.1	(Mohajeri *et al.* 2010)
	H_2O_2/Fe^{3+}		Color	78.3	
4	H_2O_2/Fe^{2+}	Coking wastewater.	phenol	95	(Chu *et al.* 2012)
			COD	44	
5	H_2O_2/Fe^{2+}	Water contaminated with CFVP.	CFVP	95	(Oliveira *et al.* 2014)
6	H_2O_2/Fe^{2+}	The textile effluent	COD	90	(Karthikeyan *et al.* 2011)
			BOD	61	
			TOC	64.1	
7	H_2O_2/Fe^{2+}	Agro-industrial wastewaters	TOC	58.8	(Martins *et al.* 2010)
8	H_2O_2/Fe^{2+}	The pharmaceutical wastewater	COD	56.4	(Martí *et al.* 2003)
9	H_2O_2/Fe^{2+}	Water contaminated Direct Blue 71	DB71 dye	94	(Ertugay & Acar 2013)
			COD	50.7	
10	H_2O_2/Fe^{2+}	Oil recovery industry wastewater.	COD	86	(Dincer *et al.* 2008)
	H_2O_2/Fe^{2+}/UV			81	
	H_2O_2/UV			39	
11	H_2O_2/Fe^{2+}	The fish canning industrial wastewater.	DOC	63	(Cristóvão *et al.* 2014)
12	H_2O_2/Fe^{2+}	Active pharmaceutical wastewaters.	COD	54	(Hussain *et al.* 2013)
13	H_2O_2/Fe^{2+}	Real effluent with COD: 1500 mg/L.	COD	45	(Kang & Hwang 2000)
#	H_2O_2/Fe^{2+}/Solar	Petroleum wastewater from SOR.	COD	74.7	This study
			TOC	59.3	

4. Comparison the results with other works

The results of this research were compared with those of other works that treated the wastewater by using the photo-Fenton method. Comparing this work with the previous works was summarized in the Table 2.

Da Rocha *et al.,* (2013) showed that polycyclic aromatic hydrocarbons and aromaticity removal of approximately 92.7 and 96.2%, respectively, from petroleum-extraction wastewater were obtained by a solar photo-Fenton like process after 420 min and solar photo-Fenton process achieved 53% COD removal.

Tony *et al.,* (2012) obtained 50% COD removal after using (H_2O_2/ Fe^{+2}/UV) method under optimal conditions; pH 3, H_2O_2/Fe^{+2} ratio 10 while the current study revealed that the solar photo-Fenton process in an AOP was more efficient in the petroleum wastewater treatment, achieving a 74.7% COD removal at conditions; pH 3.68, H_2O_2/ Fe^{+2} ratio 14. The maximum of COD removal at pH 3.68 agreed with the results found in the literature for other wastewaters treated by Fenton process, for example, Ertugay and Acar, (2013) indicated that the highest COD removal was determined 50.7% at pH 3.

5. Evaluation of the solar photo-Fenton process

To evaluate the photolytic effect on the COD and TOC removal, the photolytic process experiments were carried out under sunlight. The tubular photo reactor operated under exposure category of very high (8-11) according to a UV-index. The results revealed that the photolytic process was less efficient in the petroleum wastewater treatment, achieving an 11.5% and 9% of COD and TOC removals, respectively, at pH 3.68 after 180 min of solar irradiation as shown in Figure 8.

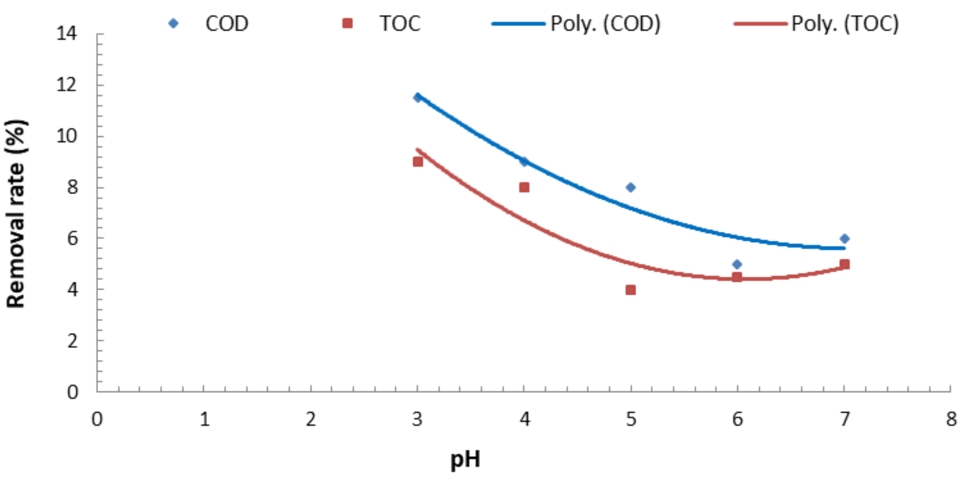

Figure 8. Effect of pH on the degradation rate of TOC & COD by the photolytic process at 180 min

Some experiments were carried out by adding 0.85 g L^{-1} Hydrogen peroxide (H_2O_2) (35% (v/v)) to evaluate the effect of the Hydrogen peroxide (H_2O_2) with solar radiation. The results revealed that 23% and 24% of COD and TOC, respectively, were removed within 180 min at pH 3.68 as shown in Figure 9. The degradation was attributed to the photochemical cleavage of H_2O_2 by solar light absorption resulting to increase rate of production hydroxyl radical (•OH) (Parsons, 2005; Oliveira *et al,.* 2012).

To evaluate the performance of employing the Fenton process in the absence of solar irradiation to treat petroleum wastewater, the Fenton experiments were carried out with adding 0.85 g L^{-1} hydrogen peroxide (H_2O_2) (35% (v/v)) and 0.06 g L^{-1} Iron sulfate hydrate ($FeO_{12}S_3$) at pH 3.68. As shown in Figure 10, Results of this process indicated that the COD removal was decreased to 61%% at pH 3.68 after 180 min, due to the lower generation of hydroxyl radical (•OH).

6. Conclusions

- In the present study, the performance of employing of solar photo-Fenton (H_2O_2/Fe^{2+}/Solar) in the AOP on degradation of TOC and COD from petroleum waste water in Sohar oil refinery in Oman are investigated.
- The general results of this work indicated that the solar photo-Fenton was a practical method to treat petroleum wastewaters, allowing achieved well removal of TOC and COD.
- The obtained optimum conditions include H_2O_2 dosage (1 g L^{-1}), Fe^{+2} dosage (0.08 g L^{-1}), pH (3) and reaction time (180 min). TOC and COD removal rates are 64 % and 78 %, respectively.
- However, the photolytic process was less efficient in the petroleum wastewater treatment, achieving an 11.5% and 9% of COD and TOC removals, respectively.
- The solar photo-Fenton process has well efficient for petroleum wastewater treatment in acidic conditions, achieving a 74.7 % COD removal at pH = 3.68, and more economic by free energy.

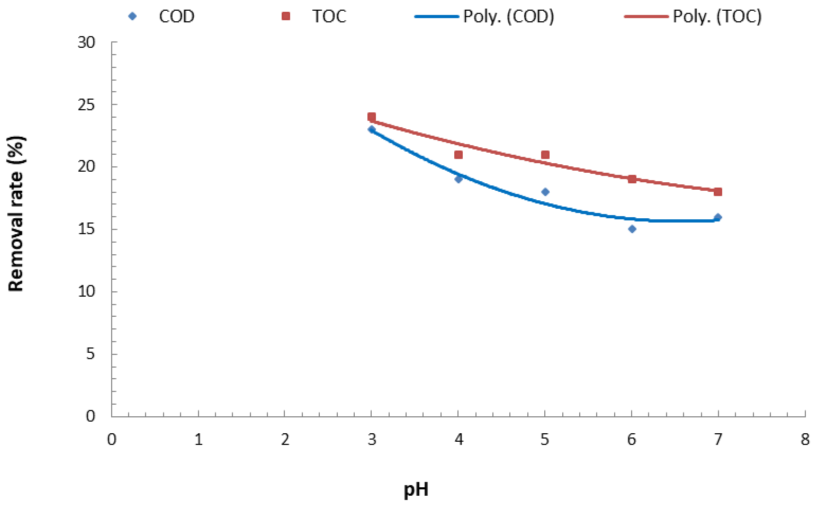

Figure 9. Effect of pH on the degradation rate of TOC and COD by the H_2O_2/solar process at 180 min

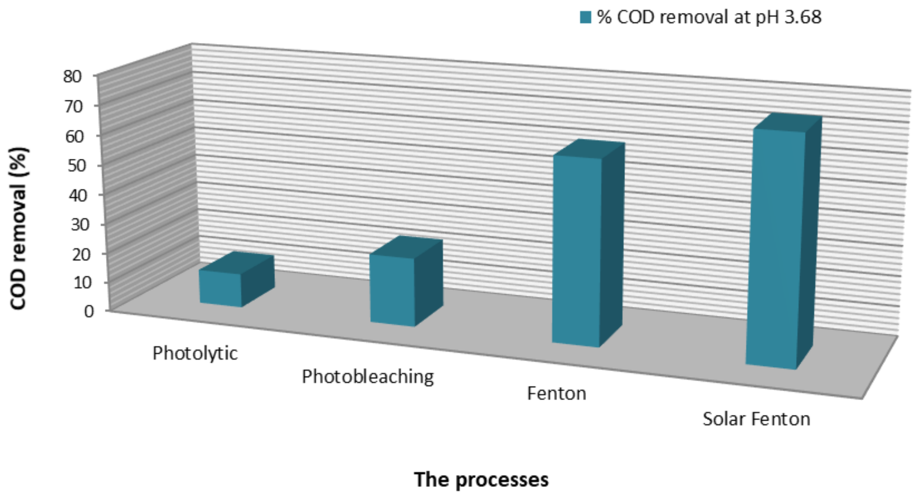

Figure 10. COD removal from petroleum wastewater under different processes

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