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Performance of different photocatalytic oxidation processes in petroleum wastewater treatment: A Comparative Study

Aljuboury D.A.D.A.[1,*], Palaniandy P.[1], Abdul Aziz H.[1], Feroz S.[2] and Abu Amr S.S.[3]

[1]School of Civil Engineering, Universiti Sains Malaysia, Malaysia

[2]Caledonian College of Engineering, Oman.

[3]Environmental Engineering Technology Department, Malaysian Institute of chemical and Bioengineering Technology, Universiti Kuala Lumpur, (UniKL, MICET), 78000, Melaka, Malaysia.

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*to whom all correspondence should be addressed:
e-mail: msc.dheeaa@yahoo.com

Abstract

The present study was conducted to compare the performance of different solar photocatalytic processes (TiO_2 photocatalysis, photo-Fenton, photo-Fenton coupled with TiO_2 photocatalysis, and photo-Fenton coupled with TiO_2/ZnO photocatalysis) for the treatment of petroleum wastewater. The removal efficiency of chemical oxygen demand (COD) is evaluated. TiO_2 dosage and pH are the main factors that improve the COD removal in the TiO_2 photocatalysis process while Fe^{+2} and H_2O_2 concentration are the main factors in photo-Fenton process. The photo-Fenton coupled with TiO_2/ZnO photocatalysis is the most efficient process for treatment of petroleum wastewater at the neutral conditions (pH 7). Therefore, no need to adjust pH during this treatment. In acidic conditions (pH<7), the photo-Fenton process is more efficient than the TiO_2 photocatalysis process while it is less efficient than the TiO_2 photocatalysis process in alkaline conditions (pH>7).

Keywords: TiO_2 photocatalysis process; Photo-Fenton process; photo-Fenton coupled with TiO_2 photocatalysis process; photo-Fenton coupled with TiO_2/ZnO photocatalysis processes; the petroleum wastewater.

1. Introduction

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 wastewater in Sohar oil refinery. 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 capability of rapid degradation of recalcitrant pollutants in the aquatic environment. They have shown high efficiency to remove the organic compounds from effluents even when they are present at low concentrations (Philippopoulos and Poulopoulos 2003; Da Silva *et al*., 2015; Masomboon *et al*., 2010; Paz *et al.,* 2013). In addition, they didn't form environmentally hazardous byproducts. Remediation of hazardous substances is attributed to hydroxyl radical, which has the potential to destroy and degrade toward organic (Hermosilla *et al*., 2009; Malato *et al.*, 2001).

When TiO_2 expose to sunlight in the TiO_2 photocatalysis, a hole in the valence band and an electron in the conduction band are generated by light induction. This hole cause the oxidation of hydroxyl ions and produce the hydroxyl radicals at the TiO_2 surface. While in the photo-Fenton process, formation of hydroxyl radicals base on reaction between Fe^{+2} and H_2O_2 under sunlight irradiation.

The AOPs have shown promising results in treatment of non-biodegradable and toxic compounds (Boundjou *et al*., 2012). They consider techniques for the treatment of polluted water because they are eco-friendly, fast, effective, and able to completely oxidize organic molecules at a low energy cost (Kwon *et al*., 2008).

The reactions with hydroxyl radicals can be triggered by several ways depending on the structure of the organic compounds, electron transfer, abstraction of hydrogen atom, and electrophilic (Philippopoulos and Poulopoulos 2003; Legrini *et al*., 1993). The major drawbacks of Fenton process are iron complexation by carboxylic intermediates. But these complexes can be photo-activated by photo-Fenton process and additional hydrogen peroxide ($HO^\bullet$) generation (Amor *et al*., 2015; Diyauddeen *et al*., 2011). Therefore, the photo-Fenton experiments are applied to treat petroleum wastewater.

The solar photo-Fenton is based on using solar radiation to increase production of hydroxyl radicals (•OH) (Amor *et al*., 2015; Fernandez *et al*., 2014; Lucas and Peres, 2009; Pignatello *et al*., 2006). Using solar energy in AOPs can reduce processing costs and make it more affordable for commercial use (Amor *et al*., 2015).

Several previous studies have reported the enhanced oxidation of contaminants by the TiO_2 photocatalysis process and the photo-Fenton coupled with TiO_2 photocatalysis. Tony *et al.,* (2009) reported that the Fenton/TiO_2/UV process achieved an 84% COD removal in the diesel oil-water emulsion while the Fenton/ZnO/UV process resulted in a reduction of about 18% in the COD removal efficiency. This result might be because the surface area of TiO_2 was more than that for ZnO. Duran and Monteagudo, (2007) found that the pH and TiO_2 concentration were the main factors for the photo-Fenton coupled with TiO_2 photocatalysis process at an acidic conditions. While Nogueira *et al.,* (2004) showed that the roles of TiO_2 was less important than that of iron and H_2O_2 in the degradation of 4CP and DCA by the TiO_2 photocatalysis process. Kim *et al.,* (2012) reported that the TiO_2 photocatalysis process increased COD removal at pH (6.5-7.5). Rossiter *et al.,* (2013) showed that the 53% COD removal was achieved by the photo-Fenton process from petroleum wastewater at an acidic conditions (pH 3.5).

The main aims for this study are as follows:

- To compare of the homogenous and the heterogeneous photocatalysis processes such as the photo-Fenton, the TiO_2 photocatalysis, the photo-Fenton coupled with TiO_2 photocatalysis, and the photo-Fenton coupled with TiO_2/ZnO photocatalysis processes.
- To assess treatment efficiencies and the main factors for these processes by "A central composite design (CCD) with response surface methodology (RSM)".

2. Materials and methods

2.1. Wastewater Characterization

The samples are collected from the point that the petroleum wastewater is just leaving the dissolved air flotation (DAF) unit in the Sohar oil refinery (SOR). Samples of the petroleum wastewater are collected in different days. Samples are transferred to the laboratory and stored under refrigeration (4 °C) until use. The petroleum wastewater characterization is determined by the quantification of pH and COD according to the Standard Methods for the Examination of Wastewater Methodology. COD is measured by COD photometer (manufactured by CHEMetrics). The pH levels are monitored by using a digital pH meter. COD is estimated before and after treatment. The characteristics of the petroleum wastewater are summarized in Table 1.

Before each analysis, samples are filtered by filter papers (0.22µm Millipore Durapore membrane, 40 ashless, Diameter 150 mm). Solar ultraviolet radiation (UV) is measured by a global UV radiometer (KIPP & ZONEN).

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

No	Parameter	Range of concentrations	Average	The standard discharge limit*
1	pH	6-8	7	6-9
2	COD (ppm)	550-1600	1075	150-200

**Wastewater discharge standard of Oman (2005)*

2.2. Materials

The catalysts are ZnO and TiO_2 Aeroxide P-25 (manufactured by Evonik Industries Co in Germany). Samples of the petroleum wastewater are collected from Sohar oil refinery (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 (95-97%) and sodium hydroxide (50%) are used to adjust the pH to the desired values.

2.3. Experimental procedure

A sketch of the photocatalysis processes is shown in Figure 1. It consists of the tubular solar reactor (four tubes (50 cm length x 2 cm inner diameter x 0.1 cm thickness)) and a glass recirculation tank (5 L), which is subjected to stirring.

The UV-Index is calculated as follow:

The output from the UV-E radiometer is taken according to ISO 17166:1999/CIE S007/E-1998. Transform the output voltage to W m^{-2} with the instruments sensitivity. Equation (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):

$$UVI=R(W\ m^{-2})*40\ (m^2\ W^{-1}) \quad (1)$$

Where:

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

The tubular photo reactor operate at a UV-index of 9 (according to Exposure category is very high) as shown in figure S1.

The solution is re-circulated through the reactor at a flow rate of about 1.5 l min^{-1} by means of a peristaltic pump. The added materials and their concentrations such as TiO_2, ZnO, H_2O_2 and Fe^{+2} depend on used process. The pH for petroleum wastewater samples is used between 3 and 8. Several sets of experiments are carried out according to CCD with RSM to determine the COD removal efficiency under the optimum operational conditions.

At the end of each run, the samples are withdrawn and then kept them at rest for 30 min in order to avoid iron precipitation in the reactor. The major iron ion is precipitated by increasing the pH of sample to (8) because the Fenton process stops at pH 8 (Abu Amr *et al.,* 2013).

Tekin *et al.,* (2006) showed that the treatment efficiency of Fenton ceased when the pH was equal to or greater than 7 because the generation of hydroxyl radicals were reduced due to lack of presence free iron ions.

The excess of hydrogen peroxide (H_2O_2) is removed by adding MnO_2. The suspension is stirred until the formation O_2 is finished (no bubbles on surface) (Herrmann, 1996). The presence of H_2O_2 normally provokes accurate COD values (Amor *et al*., 2015).

2.4. Mathematical modeling

CCD and RSM are employed in the statistical design of the experiments, data analysis, explaining the optimal conditions and assessment of the relationship among significant independent variables such as pH, catalyst dosage, and reaction time.

The adequacy of the proposed models for COD removal from the petroleum wastewaters by these processes is evaluated at the optimum conditions. Each independent variable is varied over three levels (−1, 0, +1) according to face centered CCD. The total number of experiments conducts for the four factors according to Equation (2) and for the five factors according to Equation (3) to assess the pure error and got a good estimate.

$$\text{No. of Experiments} = 2^k + 2k + 6 \quad (2)$$

$$\text{No. of Experiments} = 2^k + 2k + 8 \quad (3)$$

Where; k is the number of factors.

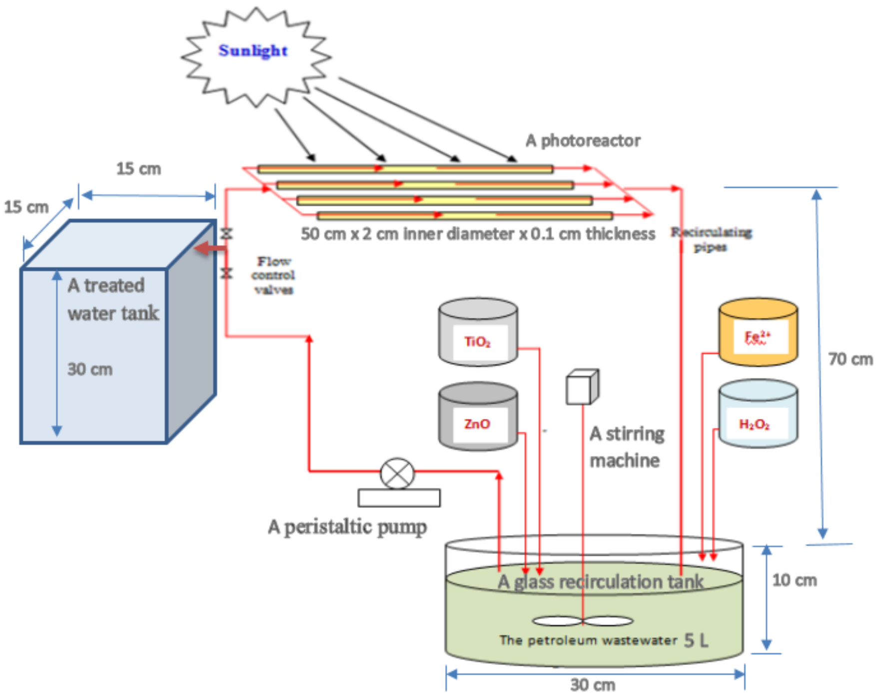


Figure 1. A sketch of the photocatalysis processes

The design consists of factorial points (2^k), axial points (2k) and 6 or 8 replications for a center point. In this work, the total numbers of experiments conduct for the four and five factors are 30 and 50, respectively. The COD removal is the dependent variable (response) during these processes.

The behavior of the system is explained through an empirical second-order polynomial model, as shown in Equation (4): (Montgomery, 2008)

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} X_i X_j + e_i \quad (4)$$

Where;

Y is the response.

X_i and X_j are the variables.

β is the regression coefficient.

k is the number of factors studied and optimize in the experiment.

e_i is the random error.

The analysis of variance (ANOVA) is used for graphical analysis of data to obtain the interaction between the process variables and the responses. The qualities of the fit polynomial models are expressed by coefficient of determination (R^2). Models terms are evaluated by the *P*-value (probability) with 95% confidence level.

All the response surface quadratic models for parameters are significant at the 5% confidence level since the *P*-values are less than 0.05. The R^2 values for the COD removal rates are greater than the cut-off (0.80) for a model with a good fit. A high 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 (Abu Amr *et al.,* 2013).

If the model terms have the *P*-value (probability) more than 0.05, they are considered a limited influence. Thus, they must be excluded from the study to improve the models according to literature. The models of COD removal are considered significant using the *F*-test at 5% significant level (Prob < 0.05).

The AP ratio is a measure of the “signal to noise ratio”. If the AP ratio values are higher than 4, they are a desirable values and confirm that the predicted models can be used to navigate the space defined by the CCD according to literature (Noordin *et al.,* 2004).

3. Results and discussion

3.1. Effect of pH

The pH not only affects the surface charge of the catalyst particles, but also influences the positions of conduction and valence bands in a semiconductor. Moreover, industrial wastewater may be discharged at various pH, which make the photocatalytic process more complicated.

Results obtained from experiments with varying pH from 3.5 to 8 are shown in figure 2. According to the results, the photo-Fenton process is more efficient than the TiO_2 photocatalysis process in acidic conditions (pH < 7) for petroleum wastewater treatment.

As shown in figure 2, the photo-Fenton coupled with TiO_2/ZnO photocatalysis process improved performance the TiO_2 photocatalysis process and the photo-Fenton process at neutral conditions (pH 7) for petroleum wastewater. By comparing the photo-Fenton process with the photo-Fenton coupled with TiO_2 photocatalysis process at neutral conditions, the COD removal is improved from 27% to 38%, respectively. This enhancement is attributed to increasing of the hydroxyl radicals (•OH) production by the presence of TiO_2 (Hermosilla *et al*., 2009).

The COD removal is observed to be faster in alkaline pH than in acidic pH range, this is attributed to negative surface of the TiO_2 with OH^- ions, which acts as an efficient trap for the photo-generated holes and produces hydroxyl radicals Equation (5) (Khan *et al.,* 2015; Jamil *et al.,* 2015).

$$OH^-_{surface} + h^+_{vb} \rightarrow OH_{surface} \quad (5)$$

Interpretation of such negative impact of the pH on the current TiO_2/organic matters interaction is a very difficult task in terms of many organic pollutants and intermediates existing in the petroleum wastewater. However, attempts have been made to explain this phenomenon. The pH-effect is related to the point of zero charge (pzc) of TiO_2 at pH 6.28 (Chou and Liao, 2005; Alaton *et al*., 2002; Shahrezaei *et al*., 2012).

In acidic media (pH < 6.2), the surface of TiO_2 is positively charged, whereas it is negatively charged under alkaline conditions (pH > 6.2) (Fernandez *et al*., 2002; Gogniat *et al*., 2006) according to Equations (6) and (Malato *et al.,* 2001);

$$TiOH + H^+ \leftrightarrow TiOH^{2+} \qquad pH<6.2 \quad (6)$$

$$TiOH + OH^- \leftrightarrow TiO^- + H_2O \qquad pH>6.2 \quad (7)$$

When the operating pH is below the pH at PZC (TiO2), the surface charge for the catalyst becomes positive and gradually exerts an electrostatic attraction force towards the negatively charged compounds. Such polar attractions between TiO2 and charged anionic organic compounds can intensify the adsorption onto the photon activated TiO2 surface for subsequent photocatalytic reactions (Chong *et al.*, 2010). This is particularly significant when the anionic organic compounds are present at a low concentration level.

At operating pH above the pH at PZC (TiO2), the catalyst surface will be negatively charged and repel the anionic compounds in water (Gogate and Pandit, 2004). Gogate and Pandit, (2004) reported that the influence of initial pH on the photocatalytic process is more complex and the observed effect is generally dependent on the type of pollutant and the PZC of the photocatalyst used during the oxidation process. The pH of the medium influences the properties of a surface charge of the photocatalyst. Thus, it has a significant effect on the electrostatic interaction between the catalyst surface and the pollutant molecules.

By comparing these results with previous studies, the results of this work are agreement with some studies. Tony *et al.,* (2009) have reported that the neutral pH of the oil-water solution was the optimum pH value for COD removal by the Fenton/ TiO_2/UV system. However, Kim *et al.,* (2012) 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 the addition of Fe^{+3} and H_2O_2 to the UV/TiO_2 system caused the negative effects at higher pH values (pH>7).

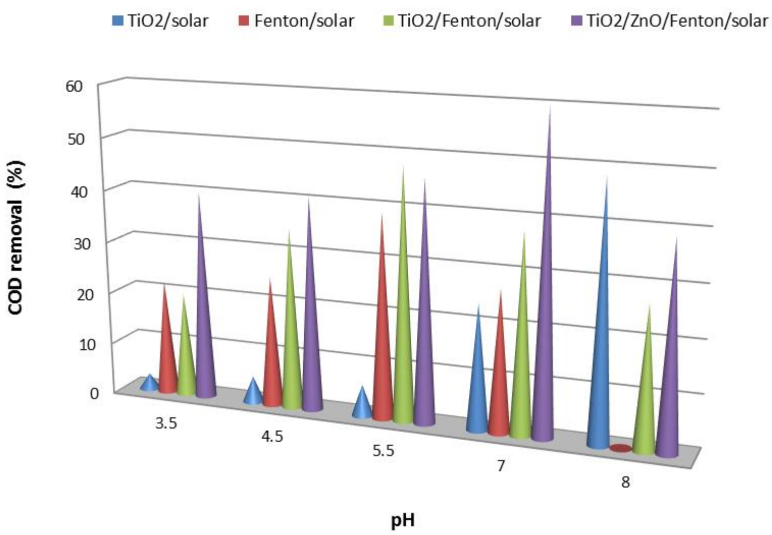


Figure 2. Comparing the four applications for COD removal under different pH values

3.2. Effect of Fenton reagent

In this study, the COD removal for the TiO_2 photocatalysis process in petroleum wastewater is improved clearly by using Fenton reagent with it in the photo-Fenton coupled with TiO_2 photocatalysis process as shown in figure 3. The rapid COD removal is attributed to high hydroxyl radical (•OH) concentrations, which exhibit reactivity toward organic compounds (De Luna *et al.,* 2013). In the photo-Fenton coupled with TiO_2 photocatalysis process, Fenton ions react with H_2O_2 to form hydroxyl radicals (•OH) as shown in Equation (8):

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + {}^{\cdot}OH \quad (8)$$

At the second stage (after 90 min) Fe^{2+} ions are decreased and 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. In addition, the excess of H_2O_2 reacts with hydroxyl radical (•OH) in result to slower rate of production hydroxyl radical (•OH) (De Luna *et al.,* 2013). Therefore, the COD removal is decreased by reducing hydroxyl radical concentrations (Tony *et al.,* 2009).

3.3. Effect of ZnO concentration

The experiments are conducted to investigate the benefits of augmenting the photo-Fenton coupled with TiO_2 photocatalysis process with ZnO. It is clear from figure 2 that the use of ZnO increases the COD removal efficiency of the photo-Fenton coupled with TiO_2/ZnO photocatalysis process at the neutral value of pH (7) for treatment of petroleum wastewater. This result may be attributed to the increase of the surface area of the photocatalysis process and an increase of the number of active sites available for adsorption (Al-Sayyed *et al.,* 1991; Alhakimi *et al.,* 2003). In addition, Several researchers have reported that ZnO has larger band-gap (3.2-3.7 eV) which favours the absorption at a wide range of solar spectrum and more light quanta than other semiconducting metal oxides (like TiO_2) (Tony *et al.,* 2009; Sakthivel *et al.,* 2003; Daneshvar *et al.,* 2004).

3.4. Effect of TiO_2 concentration

It is well known that TiO_2 has a wide band-gap (~3.2 eV) and is only excited by UV-light, thus, it is inactive under visible light irradiation. This feature of TiO_2 diminishes the utilization of solar energy as a sustainable energy source for its excitation because only 5% of the incoming solar energy on the earth's surface is in the UV range. For this reason, in recent years, in order to utilize sunlight instead of UV irradiation, studies have begun to develop the next generation of TiO_2s, well-tailored photocatalysts with high photocatalytic activities under visible light irradiation.

The COD removal in petroleum wastewater increases when the TiO_2 concentration increases until the optimum TiO_2 dosages in the TiO_2 photocatalysis process and the photo-Fenton coupled with TiO_2 photocatalysis process. The optimum TiO_2 dosages for these processes are l g l^{-1} and 0.66 g l^{-1}, 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 and the scattering of the light resulting in a reduction in production of the hydroxyl radicals (•OH) at the TiO_2 surface (Gaya and Abdullah, 2008). Thus, the higher dose of catalyst may not be useful due to reduce penetration of light and decrease the removal efficiency beyond a certain limit (Wang *et al.,* 2004; Kabir *et al.,* 2010).

3.5. Applying the optimum conditions

The optimum catalysts concentrations and pH of the solution are 0.7 g l^{-1} TiO_2, 0.3 g l^{-1} ZnO, 1.46 g l^{-1} H_2O_2, 0.01 g l^{-1} Fe^{+2} and pH (7) in the photo-Fenton coupled with TiO_2/ZnO photocatalysis process, which is the most efficient in the neutral conditions. The COD removal for this process, under the optimum conditions, is more than 60% at 180 min (RT) as shown in figure 3.

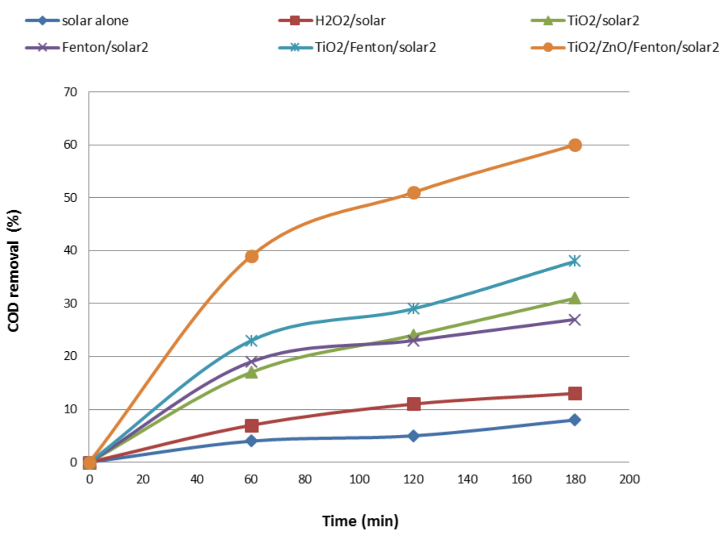


Figure 3. Comparing different processes for COD removal under pH 7

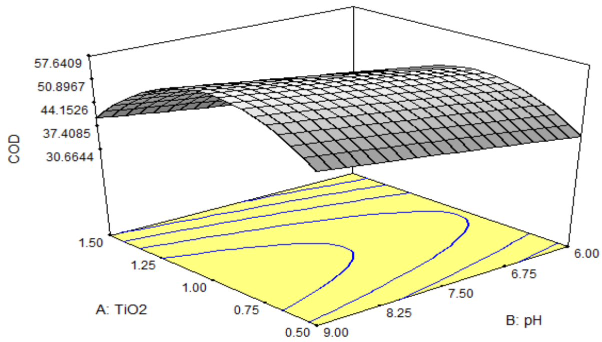
3.6. *Evaluation of the photolytic and the solar/ H_2O_2 processes*

To evaluate the photolytic effect on the COD removal, the photocatalytic experiments are carried out under sunlight. The results reveal that the photolytic process is less efficient in the petroleum wastewater treatment, achieving an 8% COD removal at pH 7 after 180 min of solar irradiation as shown in figure 3.

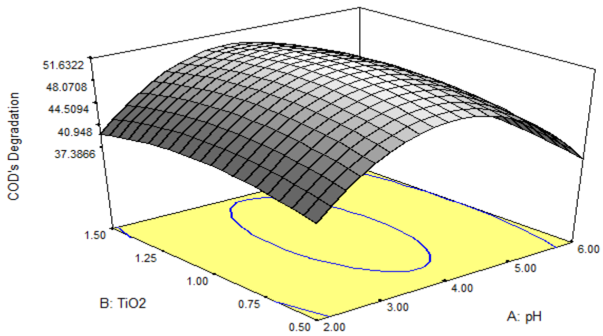
After the evaluation of the photolytic process, some experiments are carried out with adding 0.85 g L^{-1} Hydrogen peroxide (H_2O_2) (35% (v/v)), which is the optimum H_2O_2 concentration as determined previously (Aljuboury *et al.,* 2015), to evaluate the effect of the Hydrogen peroxide (H_2O_2) with solar radiation. The results reveal that 13% of COD is removed within 180 min at pH 7 as shown in figure 3. The removal is attributed to the photochemical cleavage of H_2O_2 by solar light absorption in result to increase rate of production hydroxyl radical (•OH) (Mendez-Arriaga *et al.,* 2010).

3.7. *Treatment efficiency:*

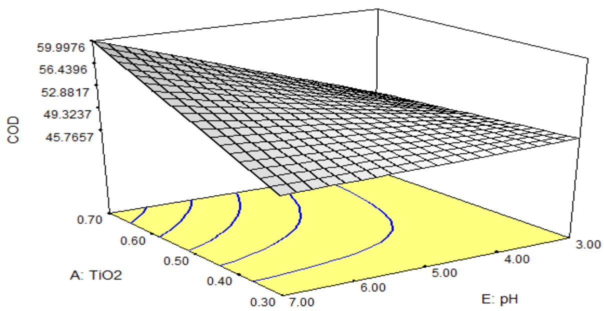
Design Expert 6.0.7 software program (a statistical software package from Stat-Ease Inc) is used to determine optimization of COD removal efficiency and to assess the interactive relationship between the independent variables and the responses of certain models. 3D surface response plots are created by Design Expert 6.0.7 software program.



(a) The solar photocatalyst of TiO_2



(b) The solar photocatalyst of TiO_2/Fenton



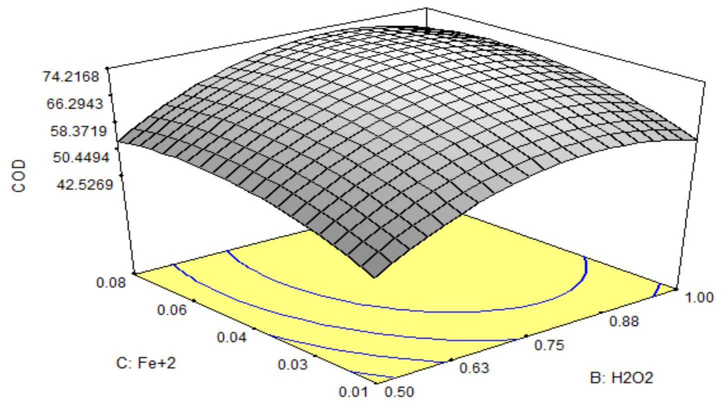
(c) The solar photocatalyst of TiO_2/ZnO/Fenton

Figure 4. Effects of TiO_2 and pH for COD removal efficiency in different processes

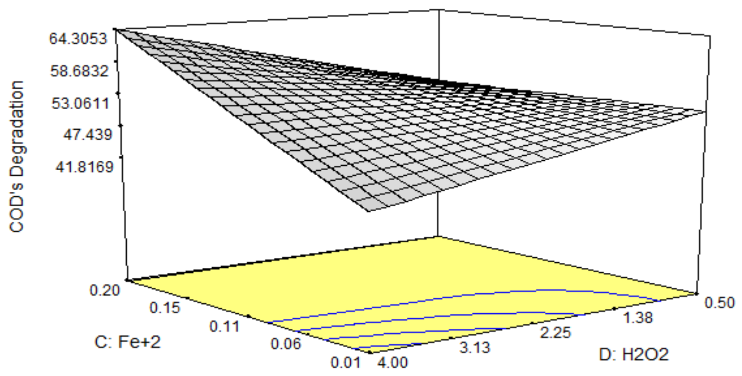
The photo-Fenton coupled with TiO_2/ZnO photocatalysis process is the most efficient neutral condition for treatment of petroleum wastewater. The highest removal rates of COD for the photo-Fenton coupled with TiO_2 photocatalysis and the photo-Fenton are in acidic conditions. However, TiO_2 photocatalysis is more efficient at alkaline conditions.

The current work reveals that The TiO_2 and pH were the two main factors that improved the COD removal for three processes (TiO_2 photocatalysis, photo-Fenton coupled with TiO_2 photocatalysis and photo-Fenton coupled with TiO_2/ZnO photocatalysis) as shown in figure 4. While the Fe^{+2} and H_2O_2 concentration are the main factors in the photo-Fenton process as shown in figure 5.

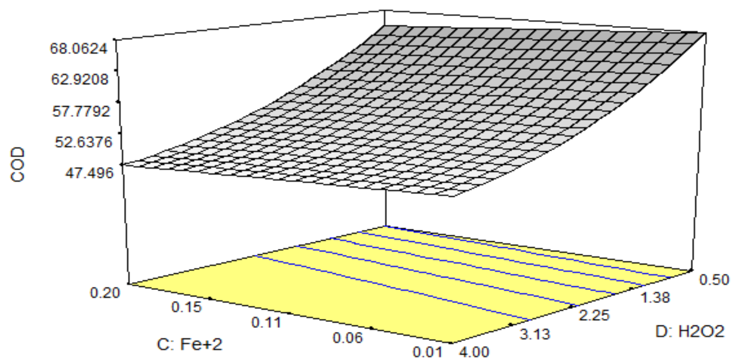
Some interactions among variables are significant. Thus, the curvature of three-dimensional surfaces is obvious in the photo-Fenton process as shown in figure 5(a). Response plots in this process have clear peaks, meaning that the optimum condition for maximum values of the responses is attributed to all four variables such as pH, H2O2 dosage, Fe+2 dosage and reaction time in the design space



(a) The solar photocatalyst of Fenton



(b) The solar photocatalyst of Fenton/TiO_2



(c) The solar photocatalyst of TiO_2/ZnO/Fenton

Figure 5. Effects of Fenton regents for COD removal efficiency in different processes

4. Conclusions

In the present study, different oxidation processes such as the photo-Fenton, the TiO_2 photocatalysis, the photo-Fenton coupled with TiO_2 photocatalysis and the photo-Fenton coupled with TiO_2/ZnO photocatalysis process are conducted to compare their performances in the treatment of petroleum wastewater by CCD with RSM. The photo-Fenton coupled with TiO_2/ZnO photocatalysis process is the most efficient in the neutral conditions to remove COD from petroleum wastewater. Therefore, no need to adjust pH during this treatment. In acidic conditions pH<7, the photo-Fenton process is more efficient than the TiO_2 photocatalysis process. While it is less efficient than the TiO_2 photocatalysis process in alkaline conditions pH>7. The TiO_2 dosage and pH are the main factors, which improve the COD removal in the TiO_2 photocatalysis processes. While the Fe^{+2} and H_2O_2 concentration are the main factors in the photo-Fenton process.

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