

# Performance of the photocatalyst and Fenton processes to treat the petroleum wastewater - A review

Dheea al deen Atallah Aljuboury<sup>1,\*</sup>, Puganeshwary Palaniandy<sup>1</sup>, Hamidi Bin Abdul Aziz<sup>1</sup>, Shaik Feroz<sup>2</sup> and Salem S. Abu Amr<sup>3</sup>

<sup>1</sup>School of Civil Engineering, Universiti Sains Malaysia, Malaysia

<sup>2</sup>Caledonian College of Engineering, Oman.

<sup>3</sup>Environmental Engineering Technology- Universiti Kuala Lumpur, (UniKL, MICET), 78000, Melaka, Malaysia.

Received: 11/12/2016, Accepted: 07/03/2017, Available online: 18/10/2017

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

## Abstract

The objective of this study is to summarize studies and investigations about advanced oxidation processes (AOPs) used for the treatment of petroleum wastewater, which mainly contained oil, organic matter and other compounds. The big difference was shown in the specification of wastewater among the investigated studies and a wide variety of pollutants at varying concentrations. The most compounds in petroleum wastewater were the mixture of hydrocarbons and inorganic compounds. Advanced oxidation processes (AOPs) have a capability of rapid degradation of recalcitrant pollutants in the aquatic environment. However, the literature regarding petroleum wastewater treatment is very little and advanced oxidation processes (AOPs) are still not being used on an industrial scale in oil refineries. Most studies were focused on the degradation of some pollutants found in the petroleum wastewater such as sulphides, ammonia, phenols and organic materials. This review focused on works that investigated advanced oxidation processes (AOPs) by monitoring general petroleum wastewater parameters such as TOC, COD, BOD, oil, and phenols. It presented an overview of photocatalytic degradation of pollutants in petroleum wastewater and highlighted the basics of these processes including the optimum parameters.

**Keywords:** Treatment of petroleum wastewater; advanced oxidation processes (AOPs); Photocatalytic processes; photo-Fenton process

## 1. Introduction

The increasing global energy demand, which expects to be 44% over the next two decades (Doggett and Rascoe, 2009), makes the processing of petroleum, which is a complex mixture of organic liquids called crude oil and natural gas, and the generation of petroleum wastewater important issues. Industrial wastewater treatment is important to study area in environmental engineering. The treatment of petroleum and petrochemical wastewater is widely studied area of research. These streams are difficult to treat due to large concentrations of oil. The composition of effluent in refinery wastewater depends on the crude

quality. It varies with the operating conditions (Benyahia *et al.*, 2006).

In the refinery, non-hydrocarbon substances were removed and the oil was broken down into its various components and blended into useful products. Thus, petroleum refineries produced large volumes of wastewater including oil well produced water brought to the surface during oil drilling, which often contain a recalcitrant compounds and rich in organic pollutants therefore could not be treated easily and difficult to be treated biologically (Vendramel S. *et al.*, 2015; Rasheed *et al.*, 2011; Asatekin A. *et al.*, 2009). Removal of pollutants produced by industrial plants was the requirement for reuse of water and obtained to environmental standards (Farajnezhad and Gharbani, 2012).

Petroleum wastewater was a major source of aquatic environmental pollution and was wastewater originating from industries primarily engaged in refining crude oil, manufacturing fuels and lubricants and petrochemical intermediates (Wake *et al.*, 2005).

Coelho *et al.*, (2006) reported that the volume of petroleum wastewater generated during processing was 0.4–1.6 times the amount of the crude oil processed. If the petroleum wastewater, which contained high organic matter, discharged into the aquatic environment, which requires 2 mg L<sup>-1</sup> from dissolved oxygen for normal life, results in decreased dissolved oxygen by the bacteria (Attiogbe *et al.*, 2007).

In anaerobic systems, the products of chemical and biochemical reactions produced displeasing colors and odors in water. So, the oxygen availability was important in water to reduce that (Attiogbe *et al.*, 2007).

These effluents were composed of grease and petroleum compounds which consist of three main hydrocarbon groups; Paraffin [very few carbon atoms (C<sub>1</sub> to C<sub>4</sub>) such as Methane (CH<sub>4</sub>), Ethane (C<sub>2</sub>H<sub>6</sub>) and Propane (C<sub>3</sub>H<sub>8</sub>)], Naphthene [such as Cyclohexane (C<sub>6</sub>H<sub>12</sub>) and Dimethyl Cyclopentane (C<sub>7</sub>H<sub>14</sub>)] and Aromatics [The more carbon atoms a hydrocarbon molecule such as Benzene (C<sub>6</sub>H<sub>6</sub>), Toluene (C<sub>7</sub>H<sub>8</sub>) and Xylene (C<sub>8</sub>H<sub>10</sub>) (Wang B., 2015). In

addition, Naphthenic acids (NAs) which are one class of compounds in wastewaters from petroleum industries that were known to cause toxic effects, and their removal from oilfield wastewater was an important challenge for remediation of large volumes of petrochemical effluents (Wang B. *et al.*, 2015).

When a crude oil contained appreciable quantities of Sulphur, it was called sour crude. So, Sour water was a specific stream of petroleum refineries, which contain slowly biodegradable compounds and toxic substances (Coelho *et al.*, 2006). Petroleum wastewaters could vary greatly in their specifications, depending on the plant configuration, operation procedures and type of oil being processed (Saïen and Nejati, 2007).

The methods of petroleum wastewater treatment need to other steps to remove the organic matter, because they transferred of contaminants from one medium to another which include Chemical oxidation (Hu G *et al.*, 2015), Biological techniques (Wang Y. *et al.*, 2015), Coagulation (Abu Hassan M. A., 2009; Farajnezhad and Gharbani, 2012; El-Naas *et al.*, 2009) and Adsorption (Al Hashemi W., 2015). In addition, new technologies have also been reported such as Microwave-assisted catalytic wet air oxidation (Sun Y. *et al.*, 2008) and Membranes (Shariati *et al.*, 2011; Yuliwati E. *et al.*, 2011).

Diyauddeen *et al.* (2011) reviewed treatment technologies for petroleum refinery effluents and showed that the petroleum refinery effluents treatment consisted of two main steps, which are pre-treatment and advanced treatment. The Biodegradation, Photocatalytic degradation, adsorption and other have been investigated with promising results. The important parameters in these treatment techniques were chemical oxygen demand (COD), biological oxygen demand (BOD), total petroleum hydrocarbon (TPH), oil and grease, sulphate and phenols. Because these methods have some disadvantages, the advanced oxidation processes (AOPs) get more attention due to their capability of rapid degradation of recalcitrant pollutants in the aquatic environment by hydroxyl radical ( $\cdot\text{OH}$ ) (Aljuboury *et al.*, 2015a; Kim J.L. *et al.*, 2012), which has a high oxidation potential (estimated to be +2.8 V) relative to other oxidants (Al-Rasheed *et al.*, 2005) and they have high efficiencies and less generation of sludge. In addition, they operated within a wide pH range.

This review focused on works that investigated advanced oxidation processes (AOPs) to treat the petroleum wastewater.

## 2. Wastewater and petroleum wastewater

The refineries are classified into either hydro-skimming unit, which includes a crude distillation unit, a de-sulphurising unit, and a reforming unit, or a complex unit, which include a catalytic cracking unit with the hydro-skimming refinery (Al Zarooni & Elshorbagy, 2006). In addition, the petrochemical plants are sometimes incorporated within the refinery complex (Wake, 2005). In general, the pollutants in wastewater could be divided into organic matter, inorganic matters and heavy metals (Tengrui *et al.*, 2007). The organic compounds and

ammonia nitrogen considered the principal chemical characteristics of environmental concern in wastewater. The COD, TOC, and BOD are used as parameters to describe organic matter in wastewater.

### 3. Petroleum wastewater generation in refineries

Transforming crude oil into useful products such as Gasoline and kerosene is achieved by the numerous refinery configurations. During these processes, the petroleum wastewater is generated in the units such as hydro-cracking, hydro-cracker flare, hydro-skimming, hydro-skimmer flare, sourwater, Condensate, Condensate flare, and the desalter. In addition, the main sources of total phenols at the refinery wastewater treatment plant are the neutralized spent caustic waste streams, the tank water drain and the desalter effluent (Al Hashemi *et al.*, 2015). Other units indirectly involve with processing such as sanitary, crude tank and laboratory water (Al Zarooni & Elshorbagy, 2006). The dominant pollutants in petroleum wastewater are normal-alkanes ( $\text{C}_{10}\text{-C}_{21}$ ), aromatics, and polycyclic hydrocarbons (Shokrollahzadeh *et al.*, 2008). In the refinery, non-hydrocarbon substances are removed and the oil is broken down into its various components and blend into useful products. Due to that, petroleum refineries produce large volumes of wastewater. In addition, the oil wells produce the petroleum wastewater during oil drilling, which often contain recalcitrant compounds and rich in organic pollutants. Therefore, the petroleum wastewater could not be treated easily and difficult to be treated biologically (Rasheed *et al.*, 2011; Vendramel *et al.*, 2015). Removal of pollutants from the petroleum wastewater is a requirement for reuse of water and obtained to environmental standards (Farajnezhad & Gharbani, 2012).

#### 3.1. Petroleum wastewater characteristics

The different types of organic materials typically in the petroleum wastewater are shown in Table 1. The most of them contented oil, grease, phenolic compounds, nitrogen, and sulphur components (Abdelwahab *et al.*, 2009; Kavitha & Palanivelu, 2004; Lathasree *et al.*, 2004; Pardeshi & Patil, 2008; Yang *et al.*, 2008).

The oil and grease in the petroleum wastewater are sticky and clog drain pipes as well as they cause unpleasant odors and corroding (Xu & Zhu, 2004). The phenolic compounds threat the environment due to their extreme toxicity and ability to remain for long periods (Abdelwahab *et al.*, 2009; Kavitha & Palanivelu, 2004; Lathasree *et al.*, 2004; Pardeshi & Patil, 2008; Yang *et al.*, 2008). The nitrogen and sulphur components in the petroleum wastewater are represented in the form of ammonia and hydrogen sulphide ( $\text{H}_2\text{S}$ ), respectively (Altaş & Büyükgüngör, 2008).

In addition, Naphthenic acids (NAs) are one class of compounds in wastewaters from petroleum industries that are known to cause toxic effects, and their removal from oilfield wastewater is an important challenge for remediation of large volumes of petrochemical effluents (Wang B. *et al.*, 2015). Due to the petroleum wastewater content high polycyclic aromatics, which are very toxic, it

was considered hazardous pollutants on the environment (Mrayyan & Battikhi, 2005; Wake, 2005).

The identification of the organic pollutants in petroleum refinery wastewater in some refineries showed that the major compounds were different fractions of petroleum aliphatic hydrocarbons (up to C<sub>10</sub>) and the well-known aromatic compounds such as benzene, toluene, and ethylbenzene (Saïen & Nejati, 2007).

Seif, (2001) showed that the maximum removal for COD and BOD were around 1400-1500 mg L<sup>-1</sup> and 25-30 mg L<sup>-1</sup>, respectively, from different sources of petrochemical wastewater by using physical treatment and concluded that separation and individual treatment for each source

was a good alternative to treatment full quantity after mixing of different sources.

(Wang B. *et al.*, 2015) reported that the percentage of aromatic naphthenic acids (NAs) in total naphthenic acids (NAs) was estimated to be 2.1-8.8% in a refinery wastewater treatment plant. These effluents were composed of grease and petroleum compounds, which consist of three main hydrocarbon groups; Paraffin [very few carbon atoms (C<sub>1</sub> to C<sub>4</sub>) such as Methane (CH<sub>4</sub>), Ethane (C<sub>2</sub>H<sub>6</sub>) and Propane (C<sub>3</sub>H<sub>8</sub>)], Naphthene [such as Cyclohexane (C<sub>6</sub>H<sub>12</sub>) and Dimethyl Cyclopentane (C<sub>7</sub>H<sub>14</sub>)], and Aromatics [The more carbon atoms a hydrocarbon molecule such as Benzene (C<sub>6</sub>H<sub>6</sub>), Toluene (C<sub>7</sub>H<sub>8</sub>) and Xylene (C<sub>8</sub>H<sub>10</sub>) (Wang B. *et al.*, 2015).

**Table 1.** Characteristics of petroleum wastewater and standard discharge limits for refinery effluents reported by various researchers

The reference	pH	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	NH <sub>3</sub> (mg/L)	Ph. (mg/L)	S <sup>2-</sup> (mg/L)	Tur. (NTU)	Oil (mg/L)	TDS (mg/L)	TOC (mg/L)
(Vendramel <i>et al.</i> , 2015)	8.3	1250	-	150	-	-	-	-	-	-	-
(Aljoubory & Senthilkumar, 2014)	6.5-9.5	550-1600	-	-	-	-	-	-	-	1200-1500	220-265
(Saber <i>et al.</i> , 2014)	6.7	450	174	150	-	-	-	-	870	-	119
(Gasim <i>et al.</i> , 2013)	8.5	7896	3378	-	13.5	-	-	-	-	-	-
(Tony <i>et al.</i> , 2012)	7.6	364	-	105	-	-	-	42	946	-	-
(Hasan <i>et al.</i> , 2012)	7	1343	846	74	-	-	-	83	240	-	398
(Farajnezhad & Gharbani, 2012)	7.5	1120	-	110	-	-	-	-	-	-	-
(Abdelwahab <i>et al.</i> , 2009)	8	80-120	40.3	22.8	-	13	-	-	-	-	-
(El-Naas <i>et al.</i> , 2009)	9.5	4050	-	80	-	-	1222	-	-	-	-
(Altaş & Büyükgüngör, 2008)	7.2-9.2	220	-	-	-	-	20	-	-	-	-
(Dincer <i>et al.</i> , 2008)	2.5	21000	8000	2580	69	-	-	-	1140	37000	-
(Zeng <i>et al.</i> , 2007)	6.5-6.8	500-1000	-	90-300	-	20	15-30	150-350	400-1000	3000-5000	-
(Demirci <i>et al.</i> , 1998)	6.5-8.5	800	350	100	-	8	17	-	3000	-	-
(Ma <i>et al.</i> , 2009) <sup>a</sup>	6-9	< 100	< 15	< 70	< 15	-	-	-	-	-	-
(Diya'uddeen <i>et al.</i> , 2011) <sup>b</sup>	6-9	< 150	< 30	< 30	-	-	< 1.0	-	-	-	-
(Aljoubory & Senthilkumar, 2014) <sup>c</sup>	6-9	< 200	< 20	< 30	< 10	< 0.1	< 1.0	-	-	< 2000	< 75

<sup>a</sup>SDL= Standard Discharge Limits, <sup>a</sup> wastewater discharge standard of China (State Environmental Protection Administration of China, 1996),

<sup>b</sup> Environmental Health Safety Guidelines (2009), <sup>c</sup> wastewater discharge standard of Oman (2005).

When a crude oil contained appreciable quantities of Sulphur, it was called sour crude. Thus, Sour water was a specific stream of petroleum refineries, which contain slowly biodegradable compounds and toxic substances (Coelho *et al.*, 2006). The petroleum wastewaters could vary greatly in their specifications, depending on the plant configuration, operation procedures, and type of oil being processed (Saïen & Nejati, 2007).

The following general conclusions can be drawn from these Characteristics of petroleum wastewater reported by various researchers as shown in Table 1; the composition of effluent in petroleum wastewater depended on the crude quality, the operating conditions, and the sources of wastewater pollutants. Thus, the big difference was shown in the specification of wastewater among the investigated studies and a wide variety of pollutants at varying concentrations. The most compounds in petroleum wastewater were the mixture of hydrocarbons such as benzene, ethylbenzene, xylenes, toluene, polyaromatic, phenol and hydrocarbons. In addition, the dissolved formation minerals were inorganic compounds, which

included heavy metals. The average sulphide concentration was about 20 mg L<sup>-1</sup>, but it was a high concentration in sour water stream, which has complex chemical compositions such as oil, phenols, sulphides, mercaptans, ammonia, cyanides and other micro-pollutants. Thus, (El-Naas *et al.*, 2009) reported that the sulphide concentration was 1222 mg/L.

Various environmental protection agencies set maximum limits of discharge for each component of the petroleum wastewater as shown in Table 1 to protect the environment from the hazardous composition in petroleum wastewater. The fuel additives, which are carcinogenic such as dichloroethane (DCE), Dichloromethane (DCM) and *t*-butyl methyl ether (tBME), are considered the most of the undegraded total petroleum hydrocarbon (Diya'uddeen *et al.*, 2011).

#### 4. Advanced oxidation processes (APOs)

##### 4.1. Principle of APOs

AOPs may be used in petroleum wastewater treatment for overall organic content reduction, specific pollutant

destruction, sludge treatment, increasing the bioavailability of recalcitrant organics and color reduction (da Silva *et al.*, 2015). AOPs depended on the generation and increasing the concentration of hydroxyl radicals (Brillas & Casado, 2002). Kim *et al.*, (2012) indicated that hydroxyl radical exhibits reactivity toward organic compounds and also an environmentally friendly oxidant because of its ability to dissociate into nontoxic and harmless products. Hydroxyl radical has high oxidation potential (1.80-0.87 V) at pH (0-14) and considers one of the most powerful oxidizers. In addition, hydroxyl radical is stronger than chlorine and chlorine dioxide (Neyens & Baeyens, 2003).

#### 4.2. Use of Hydrogen peroxide/UV

The hydroxyl radical has a high standard oxidation potential (2.80V) and considers the second strongest oxidant after fluorine (Hermosilla *et al.*, 2009). In addition, it exhibits high reaction rates compared with other conventional oxidants such as hydrogen peroxide and  $O_3$ . Hydroxyl radicals are the main reactive species which have the potential to degrade organic pollutants, the toxic chemicals, bio-refractory compounds and react with many inorganic solutes with high-rate constants (Diyaddeen *et al.*, 2011). They also react rapidly with most alkenes and aromatic compounds, which are unreactive with hydroxyl radicals. Many oxidation processes or combinations of processes to generate hydroxyl radicals have been attempted such as Fenton and electro-Fenton process or use a combination of strong oxidants like hydrogen peroxide with catalysts (Gogate & Pandit, 2004). Hydrogen peroxide ( $H_2O_2$ ) considers not only as a relatively cheap, efficient and safe oxidant and easy to degradation of various inorganic and organic pollutants (Gogate & Pandit, 2004). The effectiveness of hydrogen peroxide ( $H_2O_2$ ) to degrade recalcitrant pollutants depends on an intermediate associate to produce hydroxyl radicals (Gogate & Pandit, 2004). However,  $H_2O_2$  has very low rates of direct oxidation for complex materials if it is used alone in petroleum wastewater. So, it should be combined with other conventional oxidants such as UV light and  $O_3$  (Diyaddeen *et al.*, 2011). Due to its slow self-decomposition rate, Hydrogen peroxide ( $H_2O_2$ ) oxidation alone may not be effective enough to degrade high concentration of recalcitrant pollutants in petroleum wastewater. Therefore, the use of hydrogen peroxide ( $H_2O_2$ ) alone considers not economically favorable and requires to be used with other advanced oxidation techniques such as Fenton reagent (using activation of  $H_2O_2$  by iron salts) to synergistically enhance its oxidizing capability. The use of  $H_2O_2$  as an oxidant has been investigated in several of the works, for example, Bustillo-Lecompte *et al.*, (2015) showed that the treatment of petroleum refinery wastewater by using a bench scale UV/ $H_2O_2$  photo-reactor in batch mode achieved the highest removal of TOC of 78.38% at 45 min and a pH of 5. Saïen & Nejati, (2007) obtained the highest level of COD degradation, which was 90% COD reduction, by a relatively low catalyst concentration of 100 mg  $L^{-1}$  in a pre-treated effluent while Coelho *et al.*, (2006) revealed that using the

$H_2O_2$ ,  $H_2O_2$ /UV, UV, photocatalysis and ozonation processes did not lead to satisfactory results, reducing at most 35% of dissolved organic carbon (DOC) in the sour water stream (SWS) and they reported a 21% DOC removal in the sour water stream (SWS) at a high catalyst loading of 200 mg  $L^{-1}$  (in comparison with 100 mg  $L^{-1}$  reported by Saïen & Nejati, (2007) within 1h of irradiation time. These results might be due to the adverse effect of excess  $H_2O_2$  on the reaction.

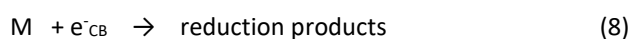
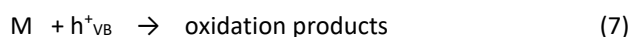
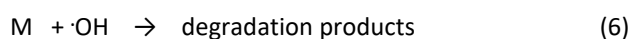
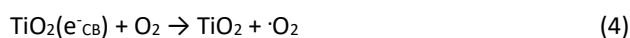
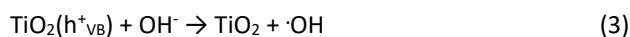
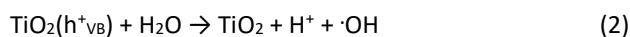
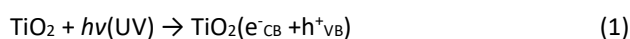
#### 4.3. The photocatalyst and Fenton processes

##### 4.3.1. The mechanism of photocatalyst and Fenton processes

The mechanism of photocatalyst and Fenton processes depended on the generation and increasing the concentration of hydroxyl radicals. The hydroxyl radical has a very high oxidation potential, high efficiencies and less generation of sludge (Al-Rasheed, 2005). In addition, it operated within a wide pH range. Under high light incident intensity, The higher catalyst activity occurs because the photons are present in excessive amounts leading to more reactive species generation and more destruction of organic compounds (Laoufi *et al.*, 2008). The intensity of UV irradiation increases the formation of hydroxyl radicals (Stepnowski *et al.*, 2002). The photons enhance photocatalytic degradation by causing favorable collision chances between photons and activatable centers (Wang *et al.*, 1999)

Understanding the roles of  $TiO_2$  and  $ZnO$  in the removal of organic compounds by photocatalyst treatment and photocatalytic mechanism helps to determine the optimal dosages for them because they are used to produce the hydroxyl radicals necessary to oxidize organic matter. These types of reactions are activated by absorption of a photon with sufficient energy (equal or higher than the band-gap energy of the catalyst). The absorption leads to a charge separation due to a promotion of an electron ( $e^-$ ) from the valence band of the semiconductor catalyst such as  $TiO_2$  or  $ZnO$  to the conduction band. Thus, a hole ( $h^+$ ) generates in the valence band (Eydivand & Nikazar, 2015; Gaya & Abdullah, 2008). Mostly, an increase in the removal efficiency is related to a rise in intensity of light due to a rise in the photon flux of electrons in the conduction band (Vohra & Tanaka, 2002).

The relevant reactions in the semiconductor surface (such as  $TiO_2$ ) governing the degradation of pollutants can be expressed as follows (Equation (1-8)) (Eydivand & Nikazar, 2015):



Where:

M is the molecule of pollutant

$h\nu$  is the photon energy required to excite the semiconductor electron from the valence band (VB) region to the conduction band (CB) region.

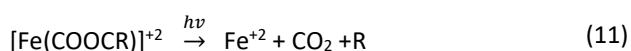
Generally, an increase in degradation is associated with an increase in light intensity due to an increase in the photon flux of electrons in the conduction band (Vohra & Tanaka, 2002). The natural solar radiation activate more electrons to jump to the conduction band from the valence band (Feroz *et al.*, 2011). The success of the photo-Fenton treatment depends on the formation of hydroxyl radicals, which are successfully produced in the presence of both iron and  $H_2O_2$ . In Fenton process, hydrogen peroxide and iron are two major chemicals.

The mechanism of Fenton process has three major steps (Equations (9-12)) (da Silva *et al.*, 2015; Krutzler & Bauer, 1999):

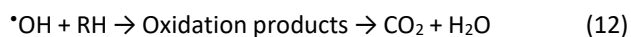
Production of hydroxyl radicals ( $\bullet OH$ ).



Reproduction of  $Fe^{+2}$  ions by energy.



Degradation of the organic compounds by hydroxyl radicals ( $\bullet OH$ ).



The complexity of intermediate compounds during the reaction and the high initial reaction rate made the study of Fenton process very difficult in industrial wastewater (Lucas & Peres, 2009).

#### 4.3.2. Parameters affecting the Fenton and the photocatalytic process.

##### Effect of pH

This parameter has a significant effect on removal the organic compounds (Alhakimi *et al.*, 2003). The pH of petroleum wastewater effects on the surface of  $TiO_2$  and forms three different species namely  $TiOH$ ,  $TiOH_2^+$  and  $TiO^-$  to account for variations in the behavior of the catalyst with pH (Yang *et al.*, 2007).

In an acidic condition, the  $TiOH$  and  $TiOH_2^+$  are the predominant species with a positively charged catalyst surface in the petroleum wastewater because the isoelectric point of  $TiO_2$  varieties between pH 4 and 6 due to the surface of the catalyst has various ionization states and influence the amount of adsorption of the substrate on the catalyst surface (Akpan & Hameed, 2009; Li *et al.*, 2006; Silva *et al.*, 2007; Yang *et al.*, 2007).

Higher degradation was obtained under acidic conditions due to strong adsorption from electrostatic attraction, for example, Topare *et al.*, (2015) showed that the maximum reduction in chemical oxygen demand (COD) of 60% from

petroleum industry wastewater was observed in acidic medium at pH 3, 50 °C and 1 g L<sup>-1</sup> catalyst concentration by employing heterogeneous photocatalytic of  $TiO_2$  process. An acidic medium can also favor organic degradation as shown by the degradation of acid brown 14 (Shahrezaei *et al.*, 2012). Shahrezaei *et al.*, (2012) reported that a maximum reduction in COD of more than 83% was achieved from petroleum refinery wastewater by using a batch circulating photocatalytic reactor in aqueous catalyst suspensions of titanium dioxide ( $TiO_2$ ) at the acidic conditions (pH 4). The hydroxyl radicals ( $\bullet OH$ ) are abundant in wastewater at high and neutral pH while positive holes are the predominant oxidation species at low pH (Akpan & Hameed, 2009). The surface under alkaline conditions becomes negatively charged. Thus, resulting in repulsion between the organic compounds and catalyst and reducing the removal efficiency due to decrease the adsorption rate (Li *et al.*, 2006). The organic compounds can be better degraded by various pH values, for example, Habibi & Vosooghian, (2005) indicated that methyl benzimidazole sulphide degradation was favored by a neutral pH while methyl phenyl sulphide was better degraded at an alkaline condition.

Pera-Titu *et al.*, (2004) explained that pH was an important parameter for the Fenton process because pH of the solution controlled the production of the hydroxyl radical and the concentration of ferrous ions. Chu *et al.*, (2012) found that the oxidation potential of hydroxyl radicals decreased with increasing pH. Removal of COD and phenol compounds depended on the initial solution pH. Oliveira *et al.*, (2014) revealed the  $H^+$  in excess reacts with the  $H_2O_2$  producing  $H_3O_2^+$ , which was stable and does not react with the  $Fe^{2+}$ , and thus there was a decreased formation of hydroxyl radicals. Furthermore, the hydroxyl radicals could be consumed by parallel reactions in the presence of an excess of  $H^+$ . Chu *et al.*, (2012) found that at pH below 3, degradation efficiency decreased. The degradation was much slower under an initial pH of 2.0. At very low pH values, iron complex species  $[Fe(H_2O)_6]^{2+}$  exist, which reacts more slowly with hydrogen peroxide than other species (Pera-Titus *et al.*, 2004).

At initial pH values (4.0-5.0), the activity of Fenton reagent was reduced due to the presence of relatively inactive iron oxyhydroxides and formation of ferric hydroxide precipitated (Rubio-Clemente *et al.*, 2015). The degradation was also slower, which was due to the formation of iron species capable of inhibiting the reaction between  $Fe^{2+}$  and  $H_2O_2$ . In addition, Oliveira *et al.*, (2014) indicated the stability of  $H_2O_2$  was lower at high pH values.

Tekin *et al.*, (2006) showed that pH did not seem to affect the treatment efficiency as long as it was equal to or greater than 7. Therefore, the pH was adjusted to 7 before Fenton's coagulation. In this situation, fewer hydroxyl radicals were generated due to the presence of fewer free iron ions. Chu *et al.*, (2012) found that at natural pH 9.1, almost no removal of phenol and COD was observed.

### Effect of dosage of catalyst

The photocatalytic efficiency of organic degradation increased with the increase of the amount of  $\text{TiO}_2$  (Laoufi *et al.*, 2008). This rise in the percentage of organic degradation may be explained by increasing the total active surface area with increasing catalyst dosage and resulted in increasing the number of hydroxyl radicals and superoxide radicals. A linear relationship exists between the initial rates of reaction and the dosages of the catalyst regardless of the catalyst conformation in photocatalytic removal (Das *et al.*, 2013). The higher catalyst activity occurs under high light incident intensity because the photons are present in excessive amounts leading to more reactive species generation and more destruction of organic compounds (Laoufi *et al.*, 2008; Wang *et al.*, 1999; Stepnowski *et al.*, 2002).

Normally, the removal efficiency rapidly increases with a rise in catalyst dosage because greater catalyst dosages result in a rise of the number of active sites existing for adsorption (Akpan & Hameed, 2009; Twesme *et al.*, 2006; Jain & Shrivastava, 2008). However, there were no significant changes beyond a certain concentration of catalyst of  $\text{TiO}_2$  and would not result in any change in the efficiency of degradation (Alhakimi *et al.*, 2003; Laoufi *et al.*, 2008). A reverse effect occurs when the  $\text{TiO}_2$  concentration increases to higher than the optimum value, the degradation rate declines due to the interference of the light by the suspension (Chakrabarti & Dutta, 2004; Ehrampoosh *et al.*, 2011). It may be due to the scattering of the light and reduction in light penetration through the effluent due to the obstruction of a large number of solid particles (Das *et al.*, 2013; Gaya & Abdullah, 2008; Singh *et al.*, 2013; Chan *et al.*, 2003). This, in turn, results in a reduction of the available active sites. Many researchers have detected a decline in organic degradation efficiency with a rise in catalyst dosage beyond a certain limit (Kabir *et al.*, 2006; Wang *et al.*, 1999). Optimal catalyst concentration was obtained at  $100 \text{ mg L}^{-1}$  by using by using the photocatalyst of  $\text{TiO}_2$  for removing aliphatic and aromatic organic pollutants in refinery wastewater (Saien & Nejati, 2007). A similar observation was made by Shahrezaei *et al.*, (2012), who reported that, at the optimum catalyst concentration of  $100 \text{ mg L}^{-1}$ , a maximum reduction in COD of more than 83% was achieved from petroleum refinery wastewater by using the photocatalyst of  $\text{TiO}_2$  while the percentage removal of COD reaches a maximum for a catalyst loading of  $1000 \text{ mg L}^{-1}$  by (Das *et al.*, 2013).

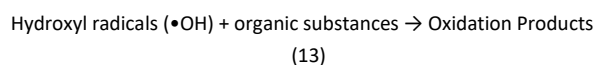
### Effect of Fenton reagent dosages

The concentration of hydroxyl radicals depends on the absolute amounts of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  in the photo-Fenton process. Rodrigues *et al.*, (2009) reported that the rate of degradation increased with an increase in the concentration of the ferrous ion. Higher dosages of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  resulted in decreased COD removal. This was explained considering that the hydroxyl radical may be scavenged by the reaction with excess  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ . Moreover, an enormous increase in the ferrous ions led to

an increase in the unutilized quantity of iron salts, which contributed to an increase of the total dissolved solids content of the effluent stream, and this was not permitted (Casero *et al.*, 1997; Kang & Hwang, 2000; Kitis *et al.*, 1999). Thus, laboratory scale studies are required to establish the optimum loading of ferrous ions to remove the organic compounds. The concentration of hydrogen peroxide plays a crucial role in deciding the efficiency of the photo-Fenton process. Usually, it is observed that the percentage degradation of the pollutant increase with an increase in the dosage of hydrogen peroxide (Kang & Hwang, 2000). However, the previous studies did not recommend the excess amount of hydrogen peroxide. Moreover, the presence of hydrogen peroxide is harmful to many of the organisms, and it affects significantly the overall degradation efficiency (Chu *et al.*, 2012).

Chu *et al.*, (2012) reported that hydrogen peroxide was the scavenging of generated hydroxyl radicals after the optimum  $\text{H}_2\text{O}_2$  dosage. Thus, the dosage of hydrogen peroxide should be utilized completely in reactions. In addition, Ertugay & Acar, (2013) indicated that the COD removal increased to 50.7% as the  $\text{H}_2\text{O}_2$  dosage increased to  $125 \text{ mg L}^{-1}$ . However, removal efficiency would decrease when  $\text{H}_2\text{O}_2$  dosage was higher than  $125 \text{ mg L}^{-1}$ . Martins *et al.*, (2010) explained that the iron load had the highest impact on TOC removal of the Phenolic wastewater after using Fenton process. The TOC removal increased as the  $\text{Fe}^{2+}$  concentration increased due to increase the production rate of the hydroxyl radicals, which led to a higher effluent mineralization level. Nevertheless, an excess of iron could have a radical scavenger effect. Oliveira *et al.*, (2014) indicated that the  $\text{Fe}^{2+}$  was responsible for speeding up the formation of hydroxyl radicals. The degradation was slower in the experiments using lower iron concentrations due to the insufficient amount of catalyst for the same amount of oxidant. Martí *et al.*, (2003) explained that the success of the Fenton treatment depended on the formation of hydroxyl radicals, which were successfully produced in the presence of both iron and  $\text{H}_2\text{O}_2$ . In Fenton process, hydrogen peroxide and iron are two major chemicals that determine the operation costs and efficacy. In order to maximize the effectiveness of the process, it was important to determine the optimal operational  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  molar ratio.

Understanding the roles of  $\text{H}_2\text{O}_2$  and iron in the removal of organic compounds by Fenton process helps to determine the optimal reagent dosages.  $\text{H}_2\text{O}_2$  and iron are used to produce the hydroxyl radicals necessary to oxidize organic substances according to the following reaction (Equation 13) (Martí *et al.*, 2003):



Consequently, particular attention must be paid to  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  dosages in order to avoid the undesired hydroxyl radicals scavenging reactions occurring in the presence of an excess of each two reagents. Martí *et al.*, (2003) reported that any addition in  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  molar ratio over the optimal Fenton ratio decreased the removal efficiency.

It seems that excessive hydrogen peroxide has a scavenging effect on hydroxyl radicals (Equation 14):



This reaction leads to the production of hydroperoxyl radical, which has weaker oxidizing power compared to hydroxyl radical (Martí *et al.*, 2003). Ertugay & Acar, (2013) explained that the excess amount of hydrogen peroxide could cause the autodecomposition of  $\text{H}_2\text{O}_2$  to oxygen and water, and the recombination of hydroxyl radicals. Thereby decreasing the concentration of hydroxyl radicals reduced the pollutant removal efficiency (Ertugay & Acar, 2013).

On the other hand, when Fenton ratio was below the optimal Fenton ratio, COD removal was decreased because of the scavenging effect of excess  $\text{Fe}^{2+}$  (Cristóvão *et al.*, 2014). It seemed that when a large amount of  $\text{Fe}^{2+}$  was available,  $\text{Fe}^{2+}$  and organic compounds compete to react with hydroxyl radicals. Thus,  $\text{Fe}^{2+}$  consumed hydroxyl radical resulting in reduced COD removal efficiency (Cristóvão *et al.*, 2014).

Dosages of Fenton reagents reported for Fenton process to treat the petroleum wastewater were very different. For example, Tony *et al.*, (2012) obtained 50% COD removal after using photo-Fenton process under the optimal  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio 10 whereas Silva *et al.*, (2015) indicated that the favorable  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  molar ratio was 22.7. The large discrepancies in reported optimal ratios of  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  were attributed to variations in the petroleum wastewater characteristics. For very high  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  values (150–268), the process was not efficient due to excess  $\text{H}_2\text{O}_2$  which led to the scavenging of radicals (Oliveira *et al.*, 2014).

#### *Effect of the initial COD concentrations*

It is found that the efficiency degradation of COD is greatly influenced with increasing the initial concentration of COD of the effluent because of the formation of hydroxyl radicals in water (Das *et al.*, 2013). A similar trend was observed when photon absorption was increased by decreasing the initial concentration of furfural solution ( $\text{C}_5\text{H}_4\text{O}_2$ ), which led to higher catalyst activation with a subsequent improvement of photocatalytic degradation (Faramarzpour *et al.*, 2009). At higher concentrations of contaminants, the clashes between the catalyst and organic contaminants are great. Thus, the higher concentrations of contaminants can improve photodegradation (Li *et al.*, 2006).

However, the percentage removal of COD decreases as the initial concentration of COD increases after a certain value. A current study by Paschoalino *et al.*, (2012) revealed that the reason for this phenomenon is likely due to the decrease in the formation of hydroxyl radicals on the catalyst surface with the increase in pollutants concentration. At the same time, the active sites decrease when the adsorbed pollutants on the catalyst surface increase because of coverage of active sites by reaction intermediate, which inhibits the direct contact between pollutants and hydroxyl radicals (Li *et al.*, 2006; Paschoalino *et al.*, 2012).

#### *Effect of reaction time*

The hydroxyl radicals ( $\bullet\text{OH}$ ) can degrade organic pollutants to intermediates, and the intermediates are further degraded to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Shahrezaei *et al.*, 2012). Thus, a required duration to complete the photo-Fenton process should be observed. According to Karthikeyan *et al.*, (2011), the percentage removal of COD increased linearly up to 4 h and was followed by a non-linear increase up to 50% in 6 h. The initial linear increased in COD reduction may be attributed to the chemical oxidation of the dissolved organics in the wastewater with hydroxyl radical. Thereafter, the reaction rate diminished as the hydrogen peroxide was consumed, which was the primary source for the generation of the hydroxyl radicals.

#### *Photocatalyst of $\text{TiO}_2$ , ZnO and $\text{TiO}_2/\text{ZnO}$*

Titanium dioxide ( $\text{TiO}_2$ ) is one of the most suitable photocatalysts for environmental application because of its biological and chemical inertness, strong oxidizing power, nontoxicity, and long-term stability against photo and chemical corrosion (Li *et al.*, 2004; Yu *et al.*, 2003).

However,  $\text{TiO}_2$  can be activated under UV light of wavelengths < 387 nm irradiation due to its large band gap of 3.2 eV (electron volt) (Yu *et al.*, 2002; Hong *et al.*, 2005). The photocatalytic activity of  $\text{TiO}_2$  usually depends on a competition between the following two processes; the ratio of the transfer rate of surface charge carriers from the interior to the surface to the recombination rate of electrons and holes. If the recombination of electrons and holes occurs too fast (<0.1 ns (nanosecond)), then there is not enough time for any other chemical reaction.

Comparing with other semiconductors, the surface charge of  $\text{TiO}_2$  are relatively long-lived (around 250 nanoseconds), which allow the electrons or holes to travel on the crystallite surface. The different types of radicals are formed on the  $\text{TiO}_2$  surface. The most common radical is hydroxyl radical ( $\bullet\text{OH}$ ), which is responsible for carrying out other chemical reactions on the surface of  $\text{TiO}_2$  (Yu *et al.*, 2005).

Oxidation occurs when a reactant loses electrons during the reaction while reduction occurs when a reactant gains electrons during the reaction. In addition, Tony *et al.*, (2009) reported that the presence of  $\text{TiO}_2$  is not only essential for the hydroxyl radicals ( $\bullet\text{OH}$ ) production, but also for the adsorption of the oil molecules on the  $\text{TiO}_2$  surface.

Consequently, particular attention must be paid to  $\text{TiO}_2$  and ZnO dosages in order to avoid the increase of turbidity in the petroleum wastewater during the photocatalyst of  $\text{TiO}_2/\text{ZnO}$  process. The turbidity hinders the absorption of the sunlight light required in this process.

Generally, the degradation of pollutants rapidly increases with increasing the concentration of catalyst (Akpan & Hameed, 2009). Another study by Jain & Shrivastava, (2008) found similar observation, and they showed that higher catalyst concentrations resulted in an increase in the number of active sites on the photocatalyst surface, which in turn increases the number of hydroxyl radicals (Das

*et al.*, 2013). However, many authors have observed a reverse effect occurred when the  $\text{TiO}_2$  concentration increased to higher than the optimum value, the degradation rate declined due to the blocking of light penetration or the scattering and the interference of the light by the suspension. This, in turn, resulted in a reduction

of the available active sites on the photocatalyst surface (Alhakimi *et al.*, 2003; Chakrabarti & Dutta, 2004; Ehrampoosh *et al.*, 2011; Gaya & Abdullah, 2008). Many optimum catalyst loadings reported by various researchers are presented in Table 2.

**Table 2.** Range of Catalyst loadings and optimum values for  $\text{TiO}_2$  to treat the petroleum wastewater reported by various researchers

No	catalyst loading	optimum catalyst loading	Ref.
1	0.25-1.5 $\text{g L}^{-1}$	1 $\text{g L}^{-1}$	(Topare <i>et al.</i> 2015)
2	2-15 $\text{g L}^{-1}$	10 $\text{g L}^{-1}$	(Shahrezaei <i>et al.</i> , 2015)
3	0.5-1.5 $\text{g L}^{-1}$	0.6 $\text{g L}^{-1}$	(Aljuboury <i>et al.</i> , 2015a)
4	0.25-2.0 $\text{g L}^{-1}$	1.2 $\text{g L}^{-1}$	(Khan <i>et al.</i> , 2015)
5	0-0.200 $\text{g L}^{-1}$	0.1 $\text{g L}^{-1}$	(Shahrezaei <i>et al.</i> , 2012)
6	0.01-0.20 $\text{g L}^{-1}$	0.1 $\text{g L}^{-1}$	(Saïen & Nejati, 2007)

The following important points should be noted from the discussion in Tables 3 and 4; the efficiencies of COD removal by the photocatalyst of  $\text{TiO}_2$  application to treat the petroleum wastewater significantly differed among the previous works due to the complexity of compounds for this type of wastewater. The majority of the studies reported that the optimal pH for the photocatalyst of  $\text{TiO}_2$  processes was strongly acidic conditions (pH 3-4).

Saïen & Nejati, (2007) reported that more than 90% COD removal was achieved by using a circulating photocatalytic ( $\text{TiO}_2/\text{UV}$ ) reactor for removing aliphatic and aromatic organic pollutants in refinery wastewater after about 4 h irradiation and hence, 73% after about only 90 min.

**Table 3.** Overview of work done in the area of photocatalyst of  $\text{TiO}_2$  applications to treat the petroleum wastewater reported by various researchers:

	The process	Removed material	Max. Removal efficiency (%)	The optimum conditions					Ref.
				pH	TiO <sub>2</sub> (mg L <sup>-1</sup> )	C <sub>0</sub> of pollutant (mg L <sup>-1</sup> )	TR (min)	T °C	
1	TiO <sub>2</sub> /UV	COD	60	3	1000	8200	-	50	(Topare <i>et al.</i> , 2015)
2	TiO <sub>2</sub> /UV	COD	50	3	10	800	120	25	(Shahrezaei <i>et al.</i> , 2015)
3	TiO <sub>2</sub> /UV	COD	40.68	4	1200	220	120	37	(Khan <i>et al.</i> , 2015)
4	TiO <sub>2</sub> /Solar	COD	48.5	8	600	1600	139	-	(Aljuboury <i>et al.</i> , 2015)
5	TiO <sub>2</sub> /UV	COD	83	4	100	220	120	45	(Shahrezaei <i>et al.</i> , 2012)
6	TiO <sub>2</sub> /UV	COD	90	3	100	180	240	45	(Saïen & Nejati, 2007)
8	TiO <sub>2</sub> /Solar	COD	60	7	1000	7500	180	40	(Singh <i>et al.</i> , 2013)
9	TiO <sub>2</sub> /UV	Phenol	80	7	200	10	120	25	(Aljubory & Senthilkumar, 2014)
10	TiO <sub>2</sub> /Solar	COD	78	8.7	1000	1200	240	-	(Aljuboury <i>et al.</i> , 2014)

Shahrezaei *et al.*, (2012) showed that a maximum reduction in COD of more than 83% was achieved from petroleum refinery wastewater by using a batch circulating photocatalytic reactor in aqueous catalyst suspensions of

titanium dioxide ( $\text{TiO}_2$ ), Degussa P25 (80% anatase, 20% rutile) at the optimum conditions (pH of 4, catalyst concentration of 100  $\text{mg L}^{-1}$ , temperature of 45  $^{\circ}\text{C}$  and reaction time of 120 min).

**Table 4.** Overview of work done in the area of  $\text{ZnO}/\text{TiO}_2$  application in recent years:

	The process	Wastewater type	Removed material	Reference
1	TiO <sub>2</sub> /ZnO/UV	aqueous solutions	methylene blue (MB) dye	(Mohabansi <i>et al.</i> , 2011)
2	TiO <sub>2</sub> /ZnO/UV	aqueous solutions	Phenol	(Anju <i>et al.</i> , 2012)
3	TiO <sub>2</sub> /ZnO/solar	aqueous solutions	Phenol	(Devipriya & Yesodharan, 2010)
4	TiO <sub>2</sub> /UV ZnO/UV	aqueous solution	(RR45) dye TOC	(Peternel <i>et al.</i> , 2007)
5	TiO <sub>2</sub> /ZnO/UV TiO <sub>2</sub> /ZnO/solar	aqueous solution of commonly used leather dyes	as acid green 16 (AG 16) dye acid brown 14 (AB 14)	(Murugesan & Sakthivel, 2002)
6	TiO <sub>2</sub> / ZnO/Air/Solar	Petroleum wastewater from SOR.	COD TOC Residual iron	(Aljuboury <i>et al.</i> , 2016a)



Khan *et al.*, (2015) revealed that the photocatalytic degradation of chemical oxygen demand (COD) from the real refinery wastewater by using  $\text{TiO}_2$ /UV achieved 40.68% but when  $\text{TiO}_2$  was combined with  $\text{H}_2\text{O}_2$  the degradation decreased to 25.35% at pH of 4, within 120 min of irradiations. Khan *et al.*, (2015) reported that  $\text{TiO}_2$  was comparatively more effective than ZnO and  $\text{H}_2\text{O}_2$  for real refinery wastewater.

Shahrezaei *et al.* (2015) proved that the degradation efficiency of COD was improved by using  $\text{TiO}_2$  with the multi-walled carbon nanotube to treat the petroleum wastewater due to the large ability of Multi-walled carbon nanotube (MWCNT) to adsorb organic molecules and to suppress the electron-hole recombination. Shahrezaei *et al.* (2015) reported that the most important factor, which limits the efficiency of photocatalyst of  $\text{TiO}_2$ , was electron-hole recombination. MWCNT was used to suppress the electron-hole recombination and enhanced the photocatalytic efficiency of titanium dioxide ( $\text{TiO}_2$ ) nanoparticles (Shahrezaei *et al.*, 2015).

Anju *et al.* (2012) reported that the removal efficiency of phenol for the combination of ZnO/ $\text{TiO}_2$ /UV process was enhanced from 37% to 46% at 90 min in aqueous solutions after using  $\text{H}_2\text{O}_2$  with this combination. Aljoubory & Senthilkumar, (2014) noted that the maximum phenol removal efficiency (%) by using a batch reactor was better than that by using a continuous reactor in  $\text{TiO}_2$ /UV process from petroleum wastewater under same condition (pH 7, initial concentration of phenol  $10 \text{ mg L}^{-1}$ , 120 min, T  $25^\circ\text{C}$  and 15 W power of UV) because the mechanism of phenol degradation could be achievable under prolonged exposures to UV irradiation. The natural solar radiation activated more electrons and enhanced them to jump from the valence band to the conduction band (Feroz *et al.*, 2011). This phenomenon is corroborated by the works of (Silva *et al.*, 2007), who observed a steady decrease in degradation of phenol and showed that decomposition percentage increased with the square root of incident light for moderate to high intensities.

#### 4.3.3 Fenton, Photo-Fenton and Fenton-like processes

The AOPs have the 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 were present at low concentrations (Silva *et al.*, 2015; Masomboon *et al.*, 2010; Paz *et al.*, 2013; Philippopoulos & Pouloupoulos, 2003). Remediation of hazardous substances was attributed to hydroxyl radical, which exhibit reactivity toward organic (Hermosilla *et al.*, 2009).

There are two Fenton reactions; the standard Fenton reaction between  $\text{Fe}^{2+}$  ions and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and the Fenton-like reaction between  $\text{Fe}^{3+}$  ions and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (Yeh *et al.*, 2008). Fenton reaction under light such as sunlight or UV is the so-called photo-Fenton and more hydroxyl radicals ( $\bullet\text{OH}$ ) are generated (Torrades *et al.*, 2004).

The organic materials in petroleum wastewater can be successfully removed by heterogeneous photocatalytic

processes such as Fenton, photo-Fenton, and electro-Fenton. Due to their potential for destroying a wide range of organic chemical materials, these processes continue to receive attention.

Solar photo-Fenton is based on using solar radiation to increase production of hydroxyl radicals ( $\bullet\text{OH}$ ) and photoactive complexes through the Fenton (Amor *et al.*, 2015; Fernandes *et al.*, 2014; Lucas *et al.*, 2012; Pignatello *et al.*, 2006). Using solar energy in AOPs could reduce processing costs and make it more affordable for commercial use (Amor *et al.*, 2015).

Several excellent reviews have been written on these processes (Akpan & Hameed, 2009; Diyaudeen *et al.*, 2011; Fujishima *et al.*, 2008; Rajeshwar *et al.*, 2008) in wastewater treatment particularly, Fenton, photo-Fenton, and electro-Fenton oxidation to remove the dissolved organic content of petroleum refinery sourwater. They showed that a combination of the Fenton and photo-Fenton processes was the oxidation method that led to the best results (Coelho *et al.*, 2006), for example, (Tony *et al.*, 2012) obtained 50% COD removal after using ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ ) method under pH 3 and  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio 10. In a study performed by da Silva *et al.* (2015), the highest oil removal achieved was 84% after 45 min of reaction by using 0.44 mM and 10 mM of ferrous ions and hydrogen peroxide, respectively. Yavuz *et al.*, (2010) showed that the most efficient method was the electro-Fenton process followed by the electrochemical oxidation using born doped diamond (BDD) anode while the electrocoagulation was found to be ineffective for the treatment of petroleum refinery wastewater (PRW). Ramteke & Gogate (2015) reported that using combined Fenton and ultrasound achieved 95% COD removal from petroleum wastewater at pH 3.

Dincer *et al.* (2008) evaluated the applications of the Fenton and photo-Fenton processes for the treatment of oil recovery industry wastewater. Under the most favorable conditions for the Fenton process (pH 3,  $\text{Fe}^{2+}$ :  $23.16 \text{ g L}^{-1}$  and  $\text{H}_2\text{O}_2$ :  $200.52 \text{ g L}^{-1}$ , a mass ratio of 8.658 for  $\text{H}_2\text{O}_2$ :  $\text{Fe}^{2+}$ ), 86% of the initial COD was removed (from 21000 to 2980  $\text{mg L}^{-1}$ ) from the petroleum wastewater. In the photo-Fenton process, the optimal ratio  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  was 168 and the optimum operating conditions was 8400  $\text{mg L}^{-1}$   $\text{H}_2\text{O}_2$ , 50  $\text{mg L}^{-1}$   $\text{Fe}^{2+}$ ,  $39^\circ\text{C}$ , and pH 3. Under these conditions, the photo-Fenton process achieved a COD removal of 81%.

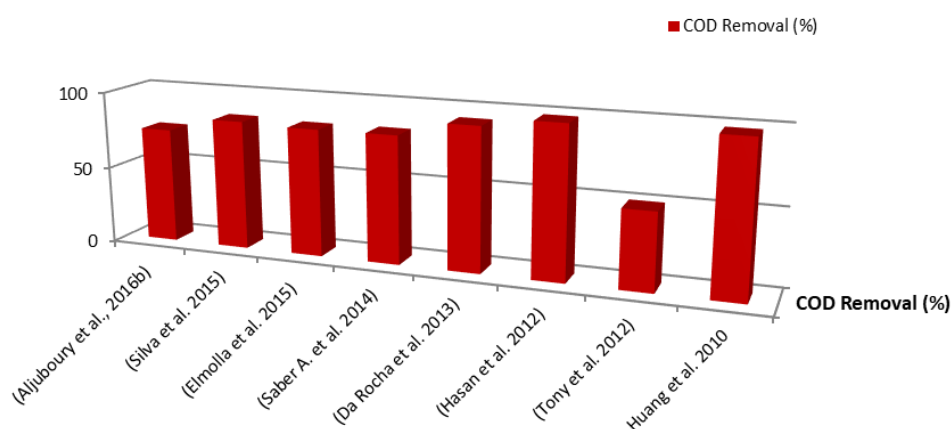
In another petroleum refinery effluent treatment study by Hasan *et al.* (2012), the maximal TOC and COD reduction achieved within 30 min of oxidation reaction were 70% and 98.1%, respectively using Fenton-like oxidation at optimized conditions of  $\text{H}_2\text{O}_2$  dosage of 1008.0 mM,  $\text{Fe}^{2+}$  dosage of 686.0 mg, pH 3, a mass ratio of 5 for  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  dosage and a molar ratio of hydrogen peroxide to the organic wastewater  $[\text{H}_2\text{O}_2]:[\text{PRE}]$  of 12 while for Fenton oxidation, they reported petroleum refinery effluent treatment was low. Saber *et al.* (2014) reported that a COD removal of more than 83 % was achieved under optimal conditions (pH 3, a mass ratio of 2.66 for  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  and ratio of 10.03 for  $\text{H}_2\text{O}_2/\text{COD}$ ) within 90 min. Davarnejad *et*

*al.* (2015) showed that maximum COD removal was around 82.55% at  $\text{H}_2\text{O}_2/\text{PRW}$  (Ratio of a mole of  $\text{H}_2\text{O}_2$  per petroleum refinery wastewater volume) of 0.04,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  molar ratio of 2.75, pH of 3.5 and reaction time of 90 min. Da Rocha *et al.*, (2013) showed that the 53% COD removal was achieved by the solar photo-Fenton process from petroleum wastewater.

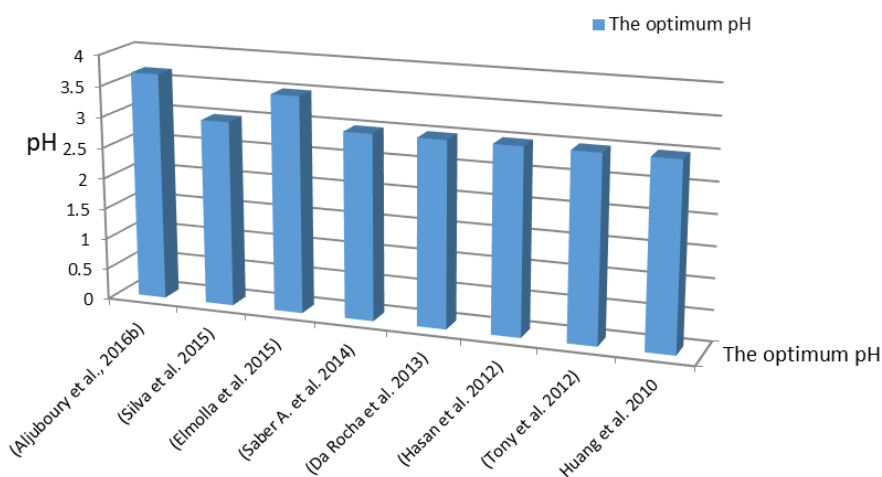
Parilti, (2010) carried out the investigation on a treatment of a petrochemical industry wastewater by the solar photo-Fenton ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{solar}$ ) process using the box-Wilson experimental design method. The solar photo-Fenton ( $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{solar}$ ) process was applied to a petrochemical refinery wastewater in Izmir, Turkey. BOD to COD ratio obtained was 0.5 by them. About 49 percent degradation of the petrochemical industry wastewater was possible. Although the Fenton process has high degradation efficiency of COD and environmental friendliness, it is

limited by the iron sludge, which needs final disposal (Pignatello *et al.*, 2006). In order to solve this issue, the Fenton process could be improved by the combined application of photocatalyst  $\text{TiO}_2$ .

The summary of the maximum percentage COD removal (%) and the optimum pH by photo-Fenton and Fenton-like applications to treat the petroleum wastewater reported by various researchers are shown in Figure 1 and Figure 2, respectively. In Fenton oxidation, organic pollutants are oxidized into  $\text{CO}_2$  and water to avoid a problem of contaminants shifting from one phase to another. Also, the operation at room temperature and atmospheric pressure prevents volatilization and discharge of unreacted wastes. Rubio-Clemente *et al.*, (2015) revealed that photo-Fenton processes were highlighted due to their fast and removal efficient for pollutants.



**Figure 1.** The maximum percentage COD removal (%) by photo-Fenton and Fenton-like applications to treat the petroleum wastewater reported by various researchers



**Figure 2.** The optimum pH for the photo-Fenton and Fenton-like applications to treat the petroleum wastewater reported by various researchers

The following important points should be noted from the discussion in Table 5; According to several studies, treatment with Fenton and photo-Fenton appeared to be an appropriate method for oxidizing recalcitrant compounds from petroleum wastewater at acidic

conditions. Use of the solar photo-Fenton in the case of commercial applications would be significantly cheaper and was also suitable to treat the petroleum wastewater. The majority of the studies reported that the optimal pH for the Fenton and photo-Fenton processes was strongly

acidic conditions (pH 3). The oxidative ability of the photo-Fenton process was greater than that of the Fenton process to treat the petroleum wastewater in the studies. Many authors showed that the optimal mass ratio of Fenton's reagent ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ) was from 2 to 10, but it sometimes was more than 200 due to the complex matrices of organic

pollutants in petroleum wastewater. Most of the previous studies did not assess the effect of a long reaction time on a stability of these methods during the treatment. Some important sides of these processes required more study such as solar intensity quantification during the solar photo-Fenton.

**Table 5.** Overview of work done in the area of Fenton, photo-Fenton and Fenton-like applications to treat the petroleum wastewater reported by various researchers:

	The process	Parameter	Max. Removal efficiency (%)	pH	The optimum conditions					Time (min)	Ref.
					$\text{H}_2\text{O}_2$		$\text{Fe}^{2+}$		$\text{H}_2\text{O}_2/\text{Fe}^{2+}$		
					ppm	mM	ppm	mM	ratio		
1	$\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{solar}$	COD	74.7	3.68	850	-	60	-	14	127	(Aljuboury et al., 2016b)
2	$\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$	TOG	84	3	-	10	-	0.44	22.7	45	(Da Silva et al., 2015)
3	$\text{H}_2\text{O}_2/\text{Fe}^{2+}$	COD	82.7	3.5	800	-	267	-	3	150	(Elmolla, 2015)
4	$\text{H}_2\text{O}_2/\text{Fe}^{2+}$	COD	83	3	4510	-	1700	-	2.7	90	(Saber et al., 2014)
5	$\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{solar}$	COD	92.7	3	-	485	0.93	-	521	420	(Da Rocha et al., 2013)
6	$\text{H}_2\text{O}_2/\text{Fe}^{3+}$	COD	98.1	3	-	1008	686	-	5	30	(Hasan et al. 2012)
		TOC	70								
7	$\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$	COD	35	3	400	-	40	-	10	90	(Tony et al., 2012)
		COD	50								
8	$\text{H}_2\text{O}_2/\text{Fe}^{3+}/\text{UV}$	COD	63	3	1080	-	5	-	216	60	(Huang et al., 2010)
		COD	98								
9	$\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$	COD	86	3	200	-	23	-	8.7	60	(Dincer et al. 2008)
		COD	81								
					8400	-	50	-	168	210	

#### 4.3.4. Photocatalyst of $\text{TiO}_2/\text{Fenton}$ and $\text{ZnO}/\text{Fenton}$

Many technics enhanced the production rate of hydroxyl radical by chemical additives ( $\text{H}_2\text{O}_2$ ), external energy (UV, sunlight), catalysts ( $\text{TiO}_2$ ) and the integration of two or more AOPs such as ( $\text{TiO}_2/\text{Fenton}/\text{sunlight}$ ) and  $\text{TiO}_2$  photocatalysis (UV)/Fenton (Kim et al., 2012). The photocatalyst of  $\text{TiO}_2$  with Fenton was applied by several

previous studies to enhance oxidation of contaminants. Tony et al. (2009) reported that a 71% and 84% COD removal were achieved at the natural pH by using Fenton/ $\text{TiO}_2/\text{UV}$  and Fenton/ $\text{TiO}_2/\text{UV}/\text{air}$ , respectively to treat the diesel oil-water emulsion while only 18% COD removal under same conditions was observed by the using Fenton/ $\text{ZnO}/\text{UV}$ . This result was attributed to the surface area of  $\text{TiO}_2$  was more than that for  $\text{ZnO}$  (Tony et al., 2009).

**Table 6.** Overview of work done in the area of Fenton/ $\text{TiO}_2$  application in recent years:

	The method						Wastewater type	Removal material	Ref.
	$\text{TiO}_2$	$\text{ZnO}$	$\text{Fe}^{+2}$	$\text{H}_2\text{O}_2$	solar	UV			
1	✓		✓	✓	✓		Milli-Q water	DNPH	(Kim et al., 2012)
2	✓	✓				✓	aqueous solutions	Phenol	(Anju et al., 2012)
3	✓		✓	✓		✓	aqueous solutions	Phenol	(Zarei et al., 2012)
4	✓	✓	✓	✓	✓	✓	oil-water emulsion	COD	(Tony et al., 2009)
5	✓		✓	✓		✓	dye polluted water	Azo dye	(Bouras & Lianos, 2008)
6	✓		✓	✓	✓		aqueous medium	4CP	(Nogueira et al., 2004)
								DCA	
								TOC	
7	✓				✓		aqueous imidacloprid	Imidacloprid	(Malato et al., 2001)
8	✓		✓	✓	✓		Pesticide wastewater	Chloropyrif	(Alalm & Tawfik, 2013)
								COD	
9	✓		✓	✓	✓		Petroleum wastewater	COD	(Aljuboury et al., 2015b)
								TOC	
								RI	
10	✓	✓	✓	✓	✓		Petroleum wastewater	COD	(Aljuboury et al., 2015c)
								TOC	
								RI	

Moreover, a recent study by Kim *et al.*, (2012) obtained 78% benzoic acid removal at circum-neutral pH (6.5-7.5) by using the  $\text{TiO}_2/\text{Fe}^{+3}/\text{H}_2\text{O}_2/\text{UV}$  system, which is very efficient in increasing production of reactive oxidants and improve the reactivity of the oxidant. However, the addition of  $\text{Fe}^{+3}$  and  $\text{H}_2\text{O}_2$  to the UV/ $\text{TiO}_2$  system at higher pH values ( $\text{pH} > 7$ ) caused the negative effects. The same results were also observed in another study by Zarei *et al.*, (2012), which they revealed that using the electro-Fenton  $\text{TiO}_2$  with  $\text{Mn}^{2+}$  under UV achieved about 70% phenol removal from aqueous solutions at 150 min under an acidic condition. They found that the pH and  $\text{TiO}_2$  concentration were the main factors while Nogueira *et al.*, (2004) showed that  $\text{TiO}_2$  concentration was less important than the roles of iron and  $\text{H}_2\text{O}_2$  in the photodegradation of 4-chlorophenol. Comparing this work with the previous works is summarized in Table 6.

## 5. Conclusions

- The petroleum wastewater was an indisputable pollution source for watercourses. It has hazardous compounds, which adversely affect the ecosystem when it is discharged into the environment. Thus, it was treated by different processes such as physical, chemical and biological (Various biological methods, both aerobic and anaerobic) treatment processes.
- The most limits of application of advances oxidation processes in wastewater treatment plants in refineries were scarce of the literature and lack of knowledge about these processes.
- Photocatalytic and photo Fenton processes, which potentially remove of the organic and inorganic matter and cost-effective technique, were an attractive and suitable for petroleum wastewater treatment at the advanced stage.
- Use of the solar photo-Fenton in the case of commercial applications would be significantly cheaper and was also suitable to treat the petroleum wastewater.
- Majority of the studies reported that the optimal pH for the Fenton and photo-Fenton processes was strongly acidic conditions.
- The oxidative ability of photo-Fenton process was greater than that of the Fenton process to treat the petroleum wastewater in the most of studies.
- The optimal mass ratio of Fenton's reagent ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ) was from 2 to 10, but it sometime was more than 200 due to the complex matrices of organic pollutants in petroleum wastewater.

## References

- Abdelwahab O., Amin N.K. and El-Ashtoukhy E-S.Z. (2009), Electrochemical removal of phenol from oil refinery wastewater, *J. Hazard Mater.*, **163**, 711-716.
- Abu Hassan M.A., Li T.P. and Noor Z.Z. (2009), Coagulation and flocculation treatment of wastewater in textile industry using chitosan, *J. Chem. Nat. Resour. Eng.*, **4**, 43-53.
- Akpan U.G. and Hameed B.H. (2009), Parameters affecting the photocatalytic degradation of dyes using  $\text{TiO}_2$ -based photocatalysts: a review, *J. Hazard. Mater.*, **170**, 520-529.
- Alhakimi G., Studnicki L.H. and Al-Ghazali M. (2003), Photocatalytic destruction of potassium hydrogen phthalate using  $\text{TiO}_2$  and sunlight: application for the treatment of industrial wastewater, *J. Photochem. Photobiol. A: Chem*, **154**, 219-228.
- Al-Hashemi W., Maraqa M.A., Rao M.V. and Hossain M.M. (2015), Characterization and removal of phenolic compounds from condensate-oil refinery wastewater, *Des. Water Treat.*, **54**, 660-671.
- Aljuboury D.D.A., Palaniandy P., Abdul Aziz H.B. and Feroz S. (2014), Organic Pollutants Removal from Petroleum Refinery Wastewater with Nanotitania Photo-catalyst and solar irradiation in Sohar Oil Refinery, *J. Innov. Eng.*, **2**(3):5, 1-12.
- Aljuboury D.D.A. and Senthilkumar R. (2014), Phenol degradation of industrial wastewater by photocatalysis, *J. Innov. Eng.*, **2**(2), 5, 1-10.
- Aljuboury D.D.A., Palaniandy P., Abdul Aziz H.B. and Feroz S. (2015a), Evaluating the  $\text{TiO}_2$  as a solar photocatalyst process by response surface methodology to treat the petroleum waste water, *Karbala Inter. J. Modern Sci.*, **1**, 78-85.
- Aljuboury D.D.A., Palaniandy P., Abdul Aziz H.B. and Feroz S. (2015b), Treatment of petroleum wastewater using combination of solar photo-two catalyst  $\text{TiO}_2$  and photo-Fenton process, *J. Environ. Chem. Eng.*, **3**, 1117-1124.
- Aljuboury D.D.A., Palaniandy P., Abdul Aziz H.B. and Feroz S. (2015c), New treatment of petroleum wastewater using the combination of solar photo-three catalysts  $\text{ZnO}$ ,  $\text{TiO}_2$  and photo-Fenton process, *Inter. J. Appl. Eng. Res.*, **10**(81), 6-14.
- Aljuboury D.D.A., Palaniandy P., Abdul Aziz H.B. and Feroz S. (2016a), Evaluating photo-degradation of COD & TOC in petroleum refinery wastewater by using the photocatalyst of  $\text{TiO}_2/\text{ZnO}/\text{Air}$  process, *Water Science & Technology*, **10**(2), 1-15.
- Aljuboury D.D.A., Palaniandy P., Abdul Aziz H. B. and Feroz S. (2016b), Evaluation of the solar photo-Fenton process to treat the petroleum wastewater by response surface methodology (RSM), *Earth Sci. J.*, **75**(4), 1-12.
- Al-Rasheed R.A. (2005) Water treatment by heterogeneous photocatalysis an overview. 4<sup>th</sup> SWCC Acquired Experience Symposium.
- Altas L. and Buyukgungor H. (2008), Sulfide removal in petroleum refinery wastewater by chemical precipitation, *J. Hazard Mater.*, **153**, 462-469.
- Al Zarooni M. and Elshorbagy W. (2006), Characterization and assessment of Al Ruwais refinery wastewater, *J. Hazard. Mater.*, **136**, 398-405.
- Amor C, Torres-Socias E.D., Peres J.A., Maldonado M.I., Oller I., Malato S. and Lucas M.S. (2015), Mature landfill leachate treatment by coagulation/flocculation combined with Fenton and solar photo-Fenton processes, *J. Hazar. Mater.*, **286**, 261-268.
- Anju S.G., Jyothi K.P., Joseph S., Suguna Y. and Yesodharan E.P. (2012), Ultrasound assisted semiconductor mediated catalytic degradation of organic pollutants in water: Comparative efficacy of  $\text{ZnO}$ ,  $\text{TiO}_2$  and  $\text{ZnO-TiO}_2$ , *Res. J. Recent Sci.*, **1**, 191-201.
- Asatekin A. and Mayes A.M. (2009), Oil Industry wastewater treatment with fouling resistant membranes containing

- amphiphilic comb copolymers, *Environ. Sci. Tech.*, **43**, 4487-4492.
- Attigbo F.K., Glover-Amengor M. and Nyadzie K.T. (2007), Correlating biochemical and chemical oxygen demand of effluents, a case study of selected industries in Kumasi, *Ghana. W. Afr. J. Appl. Ecol.*, **11**, 110-118.
- Benyahia F. (2006) Refinery wastewater treatment: a true technological challenge. 7th Annual U.A.E. University Res. Confer. 186-194.
- Bouras P. and Lianos P. (2008), Synergy effect in the combined photo-degradation of an Azo dye by titanium dioxide photocatalysis and photo-Fenton oxidation, *Catal. Lett.*, **123**, 220-225.
- Brillas E. and Casado J. (2002), Aniline degradation by electro-Fenton<sup>1</sup> and peroxi-coagulation processes using a flow reactor for waste water treatment, *Chemosphere*, **47**, 241-248.
- Bustillo-Lecompte C.F., Knight M. and Mehrvar M. (2015), Assessing the performance of UV/H<sub>2</sub>O<sub>2</sub> as a pretreatment process in TOC removal of an actual petroleum refinery wastewater and its inhibitory effects on activated sludge, *Canad. J. Chem. Eng.*, **93**, 798-807.
- Casero I., Sicilia D., Rubio S. and Perez-Bendito D (1997), Chemical degradation of aromatic amines by Fenton's reagent, *Water Res.*, **31**, 985-995.
- Chakrabarti S. and Dutta B. (2004), Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *J. Hazard Mater.*, **112**, 269-278.
- Chan A.H.C., Chan C.K.C., Barford C.J.P. and Porter J.F. (2003), Solar photocatalytic thin film cascade reactor for treatment of benzoic acid containing waste water, *Water Res.*, **37**, 1125-1135.
- Chen C., Yoza B.A., Wang Y., Wang P., Li Q.X., Guo S. and Yan G. (2015), Catalytic ozonation of petroleum refinery wastewater utilizing Mn-Fe-Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, *Environ. Sci. Pollut. Res.*, **22**, 552-562.
- Chu L., Wanga J., Dong J., Liu H. and Sun X. (2012), Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide, *Inter. Chemosphere J.*, **86**, 409-414.
- Coelho A., Castro A.V., Dezotti M. and Anna G. Jr.L.S. (2006), Treatment of petroleum refinery sourwater by advanced oxidation processes, *J. Hazard Mater. B*, **137**, 178-184.
- Correa A.X.R., Erasmo Tiepo N., Somensi C.A., Sperb R.M. and Radetski C.M. (2010), Use of ozone-photocatalytic oxidation (O<sub>3</sub>/UV/TiO<sub>2</sub>) and biological remediation for treatment of produced water from petroleum refineries, *J. Environ. Eng.*, **136**, 40-45.
- Cristovao R.O., Goncalves C., Botelho C.M., Martins R.J.E. and Boaventur R.A.R. (2014), Chemical oxidation of fish canning wastewater by Fenton's reagent, *J. Environ. Chem. Eng.*, **2**(4), 2372-2376.
- Da Rocha, O.R.S., Dantas R.F., Duarte M.M.M.B., Duarte M.M.L., Da Silva V.L. (2013), Solar photo-Fenton treatment of petroleum extraction wastewater, *Des. Water Treat.*, **51**, 28-30.
- Das L., Dutta M., Kumar J. and Basu (2013), Photocatalytic degradation of phenol from industrial effluent using titania-zirconia nanocomposite catalyst, *Inter. J. Environ. Sci.*, **4**(3), 415-431.
- Davarnejad R., Pirhadi M., Mohammadi M. and Arpanahzadeh S. (2015), Numerical analysis of petroleum refinery wastewater treatment using electro-Fenton process, *Chem. Prod. Process Model.*, **10**(1), 11-16.
- Demicri S., Erdogan B. and Oezcicmder R. (1998), Wastewater treatment at the petroleum refinery, Kirikale, Turkey using some coagulants and Turkish clays as coagulant aids, *Water Res.*, **32**, 3495-3499.
- Devipriya S.P. and Yesodharan S. (2010), Photocatalytic degradation of phenol in water using TiO<sub>2</sub> and ZnO, *J. Environ. Bio.*, **31**, 247-249.
- Diyauddeen B.H., Wan M.A., Wan D. and Abdul Aziz A.R. (2011), Treatment technologies for petroleum refinery effluents: A review, *Process Saf. Environ. Protec.*, **89**, 95-105.
- Dincer A.R., Karakaya N., Gunes E. and Gunes Y. (2008), Removal of COD from oil recovery industry wastewater by the Advanced Oxidation Processes (AOP) based on H<sub>2</sub>O<sub>2</sub>, *Glob. N. J.*, **10**, 31-38.
- Doggett T. and Rascoe A. (2009) Global Energy Demand.
- Ehrampoush M.H., Moussavi G.H.R., Ghaneian M.T., Rahimi S. and Ahmadian M. (2011), Removal of methylene blue dye from textile simulated sample using tubular reactor and TiO<sub>2</sub>/UV-C photocatalytic process, *Iran. J. Environ. Health. Sci. Eng.*, **8**, 35-40.
- Elmolla E.S. (2015), DAF-Treated Lube Oil Wastewater (DTLOWW) Treatment: Performance of Bench Scale and Pilot Scale Fenton Process, *J Civil Environ Eng.*, **5**(2), 1-5.
- El-Naas M.H., Al-Zuhair S., Al-Lobaney A. and Makhlof S. (2009), Assessment of electro-coagulation for the treatment of petroleum refinery wastewater, *J. Environ. Manage.*, **91**, 180-185.
- Ertugay N. and Acar F.N. (2013), Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: Kinetic study, *Arab. J. Chem.*, in press.
- Eydivand S. and Nikazar M. (2015), Degradation of 1,2-Dichloroethane in simulated wastewater solution: A comprehensive study by photocatalysis using TiO<sub>2</sub> and ZnO nanoparticles, *Chem. Eng. Communicat.*, **202**, 102-111.
- Farajnezhad H. and Gharbani P. (2012), Coagulation treatment of wastewater in petroleum industry using poly aluminum chloride and ferric chloride, *Inter. J. Res. Review. Appl. Sci.*, **13**, 306-310.
- Faramarzpour M., Vossoughi M. and Borghei M. (2009), Photocatalytic degradation of furfural by titania nanoparticles in a floating-bed photoreactor, *Chem. Eng. J.*, **146**, 79-85.
- Feroz S., Raut N.B. and Al-Mainmani R. (2011), Utilization of solar energy in degrading organic pollutant-A case study, *Inter. J. COMADEN*, **14**, 33-37.
- Fernandez J., Kiwi J., Lizama C., Freer J., Baeza J. and Mansilla H.D. (2002), Factorial experimental design of orange II photocatalytic discolouration, *J. Photochemistry and Photobiology A: Chem.*, **151**, 213-219.
- Fujishima A., Zhang X. and Tryk D.A. (2008), TiO<sub>2</sub> photocatalysis and related surface phenomena, *Surf. Sci. Rep.*, **63**, 515-582.
- Gasim H.A., Kutty S.R.M., Hasnain-Isa M. and Alemu L.T. (2013), Optimization of anaerobic treatment of petroleum refinery wastewater using artificial neural networks, *Res. J. Appl. Sci. Eng. Tech.*, **6**, 2077-2082.
- Gaya U.I. and Abdullah A. (2008), Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a

- review of fundamentals, progress and problems, *J. Photochem. Photobiol. C: Photochem. Rev.*, **9**, 1-12.
- Gogate P.R. and Pandit A.B. (2004a), A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.*, **8**, 501-551.
- Gogate P.R. and Pandit A.B. (2004b), A review of imperative technologies for wastewater treatment II: hybrid methods, *Adv. Environ. Res.*, **8**, 553-597.
- Habibi M.H. and Vosooghian H. (2005), Photocatalytic degradation of some organic sulfides as environmental pollutants using titanium dioxide suspension, *J. Photochem. Photobiol. A: Chem.*, **174**, 45-52.
- Hasan D.U.B., Abdul Aziz A.R. and Daud W.M.A.W. (2012), Oxidative mineralisation of petroleum refinery effluent using Fenton-like process, *Chem. Eng. Res. Des.*, **90**(2), 298-307.
- Hermosilla D., Cortijo M. and Huang C.P. (2009), Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes, *Sci. T. Environ.*, **407**, 3473-3481.
- Hong T., Wang Z.P., Cai W.M., Lu F., Zhang J., Yang Y.Z., Ma N. and Liu Y.J. (2005), Visible-light-activated nanoparticle photocatalyst of iodine-doped titanium dioxide, *Chem. Mater.*, **17**, 1548-1552.
- Hu G., Li J. and Hou H. (2015), A combination of solvent extraction and freeze thaw for oil recovery from petroleum refinery wastewater treatment pond sludge, *J. Hazard Mater.*, **283**, 832-840.
- Huang Yao-Hui, Huang Yu-Jen, Tsai Hung-Chih and Chen Hung-Ta (2010), Degradation of phenol using low concentration of ferric ions by the photo-Fenton process, *J. Taiwan Ins. Chem. Eng.*, **41**(6), 699-704.
- Jain R. and Shrivastava M. (2008), Photocatalytic removal of hazardous dye cyanosine from industrial waste using titanium dioxide, *J. Hazard. Mater.*, **152**, 216-220.
- Kabir M.F., Vaisman E., Langford C.H. and Kantzas A. (2006), Effects of hydrogen peroxide in a fluidized bed photocatalytic reactor for wastewater purification, *Chem. Eng. J.*, **118**, 207-212.
- Kang Y.W. and Hwang K.Y. (2000), Effects of reaction conditions on the oxidation efficiency in the Fenton process, *Water Res.*, **34**, 2786-2790.
- Karthikeyan S., Titus A., Gnanamani A., Mandal A.B. and Sekaran G. (2011), Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes, *Des. J.*, **2**, 438-445.
- Kavitha V. and Palanivelu K. (2004), The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, *Chemosphere*, **55**, 1235-1243.
- Khan W.Z., Najeeb I., Tuiyebayeva M. and Makhtayev Z. (2015), Refinery wastewater degradation with titanium dioxide, zinc oxide, and hydrogen peroxide in a photocatalytic reactor, *Pro. S. Environ. Protect.*, **9**, 479-486.
- Kim J.L., Leea H. and Lee C. (2012), Synergistic effects of TiO<sub>2</sub> photocatalysis in combination with Fenton-like reactions on oxidation of organic compounds at circumneutral pH, *Appl. Catal. B: Environ.*, **115**, 219-224.
- Kitis M., Adams C. and Daigger G. (1999), The effects of Fenton's reagent pre-treatment on the biodegradability of non-ionic surfactants, *Water Res.*, **33**, 2561-2568.
- Krutzler T. and Bauer R. (1999), Optimization of a photo-Fenton prototype reactor, *Chemosphere*, **38**, 2517-2532.
- Laoufi N.A. (2008), The degradation of phenol in water solution by TiO<sub>2</sub> photocatalysis in a helical reactor, *Global N. J.*, **10**, 404-418.
- Lathasree S., Rao N., Sivashankar B., Sadasivam V. and Rengaraj K. (2004), Heterogeneous photo catalytic mineralization of phenols in aqueous solutions, *J. Mol. Catal. A: Chem.*, **223**, 101-105.
- Li Y., Yan L., Xiang C. and Hong L.J. (2006), Treatment of oily wastewater by organic-inorganic composite tubular ultrafiltration (UF) membranes, *Des.*, **196**, 76-83.
- Li F.B., Li X.Z. and Hou M.F. (2004), Photocatalytic degradation of 2-mercapto-benzothiazole in aqueous La<sup>3+</sup>-TiO<sub>2</sub> suspension for odor control, *Appl. Catal. B*, **48**, 185-194.
- Lin H.T. (2005), Photocatalysis in a novel semiconducting optical fiber monolithic reactor for wastewater treatment. PhD Thesis, Louisiana State University.
- Lucas M.S., Peres J.A., Amor C., Prieto-Rodriguez L., Maldonado M.I. and Malato S. (2012), Tertiary treatment of pulp mill wastewater by solar photo-Fenton, *J. Hazard. Mater.*, **225**, 173-181.
- Lucas M.S. and Peres J.A. (2009), Removal of COD from olive mill wastewater by Fenton's reagent: kinetic study, *J. Hazard. Mater.*, **168**, 1253-1259.
- Ma F., Guo J.-B., Zhao L.-J., Chang C.-C. and Cui D. (2009), Application of bio-augmentation to improve the activate sludge system into the contact oxidation system treatment petrochemical wastewater, *Bioresour. Tech.*, **100**, 597-602.
- Malato S. and Caceres J. (2001), Degradation of imidacloprid in water by photo-Fenton and TiO<sub>2</sub> photocatalysis at a solar pilot plant: A comparative study, *Environ. Sci. Technol.*, **35**, 4359-4366.
- Martinez N.S.S., Fernandez J.F., Segura X.F. and Escola A.S.F. (2003), Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent, *J. Hazard. Mater. B*, **101**, 315-322.
- Masomboon N., Chen C.W., Anotai J. and Lu M.C. (2010), A statistical experimental design to determine o-toluidine degradation by the photo-Fenton process, *Chem. Eng. J.*, **159**, 116-122.
- Mohabansi N.P., Patil V.B. and Yenkie N. (2011), A comparative study on photo degradation of methylene blue dye effluent by advanced oxidation process by using TiO<sub>2</sub>/ZnO photo catalyst, *Rasayan. J. Chem.*, **4**, 814-819.
- Mrayyana B. and Battikhi M.N. (2005), Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge, *J. Hazard. Mater.*, **120**, 127-134.
- Murugesan V. and Sakthivel S. (2002), Photocatalytic degradation of leather dyes in aqueous solution using solar/UV illuminated TiO<sub>2</sub>/ZnO. Proceedings of International Symposium on Environmental Pollution Control and Waste Management (EPCOWM'2002), 654-659.
- Neyens E. and Baeyens J. (2003), A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.*, **98**, 33-50.
- Nogueira R.F.P., Trovo A.G. and Paterlini W.C. (2004), Evaluation of the combined solar TiO<sub>2</sub>/photo-Fenton process using multivariate analysis, *Water Sci. Technol.*, **49**, 195-200.
- Oliveira C., Alves A. and Madeira L.M. (2014), Treatment of water networks (waters and deposits) contaminated with chlorfenvinphos by oxidation with Fenton's reagent, *Chem. Eng. J.*, **241**, 190-199.

- Pardeshi S.K. and Patil A.B. (2008), A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy, *Solar Energy*, **82**, 700-705.
- Parilti N.B. (2010), Treatment of a petrochemical industry wastewater by a solar oxidation process using the Box-Wilson experimental design method, *Ekoloji*, **19**, 9-15.
- Paschoalino F.C.S., Paschoalino M.P., Jordao E. and Jardim W.F. (2012), Evaluation of TiO<sub>2</sub>, ZnO, CuO and Ga<sub>2</sub>O<sub>3</sub> on the photocatalytic degradation of phenol using an annular-Flow photocatalytic reactor, *Open J. Phys. Chem.*, **2**, 135-140.
- Pera-Titus M., Garcia-Molina V., Banos M., Gimenez J. and Esplugas S. (2004), Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B*, **47**, 219-256.
- Peternel I.T., Koprivanac N., Bozic A.M.L. and Kusic H.M. (2007), Comparative study of UV/TiO<sub>2</sub>, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in aqueous solution, *J. Hazard. Mater.*, **148**, 477-484.
- Paz D.S., Foletto E.L., Bertuol D.A., Jahn S.L., Collazzo G.C., Silva S.S., Chiavone-Filho O. and Nascimento C.A.O. (2013), CuO/ZnO coupled oxide films obtained by the electro-deposition technique and its photocatalytic activity in phenol degradation under solar irradiation, *Water Sci. Tech.*, **68**, 1031-1036.
- Philippopoulos C.J. and Pouloupoulos S.G. (2003), Photo-assisted oxidation of an oily wastewater using hydrogen peroxide, *J. Hazard. Mater.*, **98**, 201-210.
- Pignatello J.J., Oliveros E. and MacKay A. (2006) Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.*, **36**, 1-84.
- Rajeshwar K., Osugi M.E., Chanmanee W., Chenthamarakshan C.R., Zanon M.V.B., Kajitvichyanukul P. and Krishnan-Ayer R. (2008), Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media, *J. Photochem. Photobiol. C: Photochem. Rev.*, **9**, 171-192.
- Ramteke L.P. and Gogate P.R. (2015), Treatment of toluene, benzene, naphthalene and xylene (BTNXs) containing wastewater using improved biological oxidation with pretreatment using Fenton/ultrasound based processes, *J. Indus. Eng. Chem.*, **28**, 247-260.
- Rasheed Q.J., Pandian K. and Muthukumar K. (2011), Treatment of petroleum refinery wastewater by ultrasound-dispersed nanoscale zero-valent iron particles, *Ultrason. Sonochem.*, **18**, 1138-1142.
- Rodrigues C., Madeira L. and Boaventura R. (2009), Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design, *J. Hazard. Mater.*, **164**, 987-994.
- Rubio-Clemente A., Chica E. and Penuela G.A. (2015), Petrochemical wastewater treatment by photo-Fenton process, *Water Air Soil Pollut.*, **226**, 61-79.
- Saber A., Hasheminejad H., Taebi A. and Ghaffari G. (2014), Optimization of Fenton-based treatment of petroleum refinery wastewater with scrap iron using response surface methodology, *Appl. Water Sci.*, **4**, 283-290.
- Saien J. and Nejati H. (2007), Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions, *J. Hazard. Mater.*, **148**, 491-495.
- Seif H. (2001) Physical treatment of petrochemical wastewater, 6<sup>th</sup> Inter. Water Tech. Confer. IWTC, 598-607.
- Shahrezaei F., Mansouri Y., Zinatizadeh A.A.L. and Akhbari A. (2012), Process modeling and kinetic evaluation of petroleum refinery wastewater treatment in a photocatalytic reactor using TiO<sub>2</sub> nanoparticles, *Powder Tech.*, **221**, 203-212.
- Shahrezaei F., Pakravan P., Hemati A.A., Pirsaeheb M. and Mansouri A.M. (2015), Preparation of multi-walled carbon nanotubedoped TiO<sub>2</sub> composite and its application in petroleum refinery wastewater treatment, *Des. Water Treat.*, **13**, 1-10.
- Shariati S.R.P., Bonakdarpour B., Zare N. and Ashtiani F.Z. (2011), The effect of hydraulic retention time on the performance and fouling characteristics of membrane sequencing batch reactors used for the treatment of synthetic petroleum refinery wastewater, *Biores. Tech.*, **102**, 7692-7699.
- Shokrollahzadeh S., Azizmohseni F., Golmohammad F., Shokouhi H. and Khademhaghighat F. (2008), Biodegradation potential and bacterial diversity of a petrochemical wastewater treatment plant in Iran, *Biores. Tech.*, **99**, 6127-6133.
- Silva S.S., Chiavone-Filho O., Neto E.L.B. and Foletto E.L. (2015), Oil removal from produced water by conjugation of flotation and photo-Fenton processes, *J. Environ. Manage.*, **147**, 257-263.
- Silva A.M.T., Nouli E., Xekoukoulotakis N.P. and Mantzavinos D. (2007), Effect of key operating parameters on phenols degradation during H<sub>2</sub>O<sub>2</sub>-assisted TiO<sub>2</sub> photocatalytic treatment of simulated and actual olive mill wastewaters, *Appl. Catal. B: Environ.*, **73**, 11-22.
- Singh C., Chaudhary R. and Gandhi K. (2013), Preliminary study on optimization of pH, oxidant and catalyst dose for high COD content: solar parabolic trough collector, *Iran. J. Environ. H. Sci. Eng.*, **10**, 2-10.
- Stepnowski P., Siedlecka E.M., Behrend P. and Jastorff B. (2002), Enhanced photo-degradation of contaminants in petroleum refinery wastewater, *Water Res.*, **36**, 2167-2172.
- Sun Y., Zhang Y. and Quan X. (2008a), Treatment of petroleum refinery wastewater by microwave-assisted catalytic wet air oxidation under low temperature and low pressure, *Separ. Purific. Tech.*, **62**, 565-570.
- Tekin H., Bilkay O., Ataberk S.S., Balta T.H. and Ceribasi I.H. (2006), Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, *J. Hazard. Mater.*, **136**, 258-265.
- Tengrui L., Al-Harbawi A.F., Bo L.M. and Jun Z. (2007), Characteristics of nitrogen removal from old landfill leachate by sequencing batch biofilm reactor, *Americ. J. Appl. Sci.*, **4**, 211-214.
- Tony M.A., Patrick J., and Purcell Yaqian Z. (2012), Oil refinery wastewater treatment using physicochemical, Fenton and Photo-Fenton oxidation processes, *J. Environ. Sci. Heal. A.*, **47**, 435-440.
- Tony M.A., Zhao Y.Q., Purcell P.J. and El-Sherbiny M.F. (2009), Evaluating the photo-catalytic application of Fenton's reagent augmented with TiO<sub>2</sub> and ZnO for the mineralization of an oil-water emulsion, *J. Environ. Sci. Health A*, **44**(5), 488-493.
- Topare N.S., Joy M., Joshi R.R., Jadhav P.B. and Kshirsagar L.K. (2015), Treatment of petroleum industry wastewater using TiO<sub>2</sub>/UV photocatalytic process, *J. Indian Chem. Soc.*, **92**, 219-222.
- Torrades J., Garcia M., Garcia H.J.A, Domenech X. and Peral J. (2004), Decolorization and mineralization of commercial reactive dyes under solar light assisted photo-Fenton conditions, *Sol. Energy*, **77**, 573-581.

- Twesme T.M., Tompkins D.T., Anderson M.A. and Root T.W. (2006), Photocatalytic oxidation of low molecular weight alkanes: observations with  $\text{ZrO}_2\text{-TiO}_2$  supported thin films, *Appl. Catal. B: Environ.*, **64**, 153-160.
- Vendramel S., Bassin J.P., Dezotti M and Sant'Anna Jr G.L. (2015), Treatment of petroleum refinery wastewater containing heavily polluting substances in an aerobic submerged fixed-bed reactor, *Environ. Tech.*, **36**, 2052-205.
- Vohra M.M. and Tanaka K. (2002), Photocatalytic degradation of nitrotoluene in aqueous  $\text{TiO}_2$  suspension, *Water Res.*, **36**, 59-64.
- Wake H. (2005), Oil refineries: a review of their ecological impacts on the aquatic environment, *Estuar. Coast Shelf Sci.*, **62**, 131-140.
- Wang Y., Wang Q., Min L, Yingnan Y., Wei H., Guangxu Y. and Shaohui G. (2016), An alternative anaerobic treatment process for treatment of heavy oil refinery wastewater containing polar organics, *Biochem. Eng. J.*, **105**, 44-51.
- Wang B., Yi W., Yingxin G., Guomao Z., Min Y., Song W. and Jianying H. (2015), Occurrences and behaviors of Naphthenic Acids in a petroleum refinery wastewater treatment plant, *Environ. Sci. Technol.*, **49**, 5796-5804.
- Wang K.H., Hsieh Y.H., Ko R.C. and Chang, C.C. (1999), Photocatalytic degradation of wastewater from manufactured fiber by titanium dioxide suspensions in aqueous solution, *Environ. Int.*, **25**, 671-676.
- Xu X. and Zhu X. (2004), Treatment of refractory oily wastewater by electro-coagulation process, *Chemosphere*, **56**, 889-894.
- Yang, X. (2008) Sol-gel synthesized nano-materials for environmental applications. Ph.D. thesis, Kansas State University.
- Yang S.-y., Chen Y.-y., Zheng J.-g. and Cui, Y.-j. (2007), Enhanced photocatalytic activity of  $\text{TiO}_2$  by surface fluorination in degradation of organic cationic compound, *J. Environ. Sci.*, **19**, 86-89.
- Yavuz Y., Koparal A.S. and Ogutveren U.B. (2010), Treatment of petroleum refinery wastewater by electrochemical methods, *Des.*, **258**, 201-205.
- Yeh C.K.J., Hsu C.Y., Chiu C.H. and Huang K.L (2008), Reaction efficiencies and rate constants for the goethite-catalyzed Fenton-like reaction of NAPL-form aromatic hydrocarbons and chloroethylenes, *J. Hazard. Mater.*, **151**, 562-569.
- Yuliwati E., Ismail A.F., Matsuura T., Kassim M.A. and Abdullah M.S. (2011) Effect of modified PVDF hollow fiber submerged ultrafiltration membrane for refinery wastewater treatment, *Des.*, **283**, 214-220.
- Yu G., Yu J.C., Ho W.K., Leung M.K.P., Cheng B., Zhang G.K. and Zhao X.J. (2003), Effects of alcohol content and calcination temperature on the textural properties of bimodally mesoporous titania, *Appl. Catal.*, **A255**, 309.
- Yu J.C., Yu J.G., Ho W.K., Jiang Z.T. and Zhang L.Z. (2002), Effects of Fe doping on the photocatalytic activity and microstructures of nanocrystalline  $\text{TiO}_2$  powders, *Chem. Mater.*, **14**, 3808-3816.
- Zarei M., Khataee A., Fathinia M., Seyyednaji F. and Ranjbar H. (2012), Combination of nanophotocatalysis with electro-Fenton-like process in the removal of phenol from aqueous solution: GC analysis and response surface approach, *Int. J. Ind. Chem.*, **3**, 27-28.
- Zeng Y., Yang C., Zhang J. and Pu W. (2007), Feasibility investigation of oily wastewater treatment by combination of zinc and PAM in coagulation /flocculation, *J. Hazard. Mater.*, **147**, 991-996.