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Review

Treatment technologies for petroleum refinery effluents: A review

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ABSTRACT

This paper presents a brief account of different technologies used for the treatment of petroleum refinery effluents (PRE). Broadly, PRE treatment is accomplished in two stages, namely, a series of pre-treatment steps, in which suspended matter, oil and grease are reduced, and an advanced stage, in which wastewater contaminants are decreased to certain acceptable discharge limits. Photocatalytic degradation techniques have been widely used in water and wastewater treatment. However, the literature regarding PRE treatment is scarce, and the technique is still not being utilised on an industrial scale in refineries. This is largely due to limited research findings discussing PRE treatments. Most researches are focused on treating singular contaminants found in PRE, e.g., phenols, sulphides, oil, grease and other organic components. This review focused on works that investigated PRE treatment by monitoring general refinery wastewater parameters, namely, chemical oxygen demand (COD), biological oxygen demand (BOD), total petroleum hydrocarbon (TPH), oil and grease (O&G), sulphate and phenols at the advanced treatment steps. This paper presents an overview of photocatalytic degradation and discusses published works with the goal of presenting the technique as an attractive and viable process unit. If optimised, this process has great potential for replacing other separation and degradation treatment approaches employed at the advanced treatment stage for PRE.

Keywords: Photocatalytic degradation; Petroleum effluent; Environmental pollution

Contents

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1. Introduction

Petroleum refinery effluents (PRE) are wastes originating from industries primarily engaged in refining crude oil and manufacturing fuels, lubricants and petrochemical intermediates (Harry, 1995). These effluents are a major source of aquatic environmental pollution (Wake, 2005). The effluents are composed of oil and grease along with many other toxic organic compounds. Although concerted efforts have been made to replace fossil fuels, crude oil remains an important raw material. The need to satisfy the ever-increasing global energy demand, which is expected to soar by 44% over the next two decades (Doggett and Rascoe, 2009), makes the processing of crude oil and the generation of PRE globally important issues.

The process of refining crude oil consumes large amounts of water. Consequently, significant volumes of wastewater are generated (Coelho et al., 2006). Coelho et al. (2006) reported that the volume of PRE generated during processing is 0.4–1.6 times the amount of the crude oil processed. Thus, based on the current yield of 84 million barrels per day (mbpd) of crude oil, a total of 33.6 mbpd of effluent is generated globally (Doggett and Rascoe, 2009). World oil demand is expected to rise to 107 mbpd over the next two decades, and oil will account for 32% of the world's energy supply by 2030. Biofuels, including ethanol and biodiesel, are expected to account for 5.9 mbpd by 2030, and the contributions from renewable energy sources like wind and solar power are estimated to be 4–15% (Doggett and Rascoe, 2009; Marcilly, 2003). These data clearly indicate that effluents from the oil industry will continually be produced and discharged into the world's main water bodies.

These pollutants pose serious toxic hazards to the environment. PRE can vary greatly depending on the type of oil being processed, the plant configuration, and operation procedures (Saien and Nejati, 2007). They enter into waterways and adversely affect water quality.

Methods for PRE treatment include coagulation (Demirci et al., 1997; El-Naas et al., 2009b), adsorption (El-Naas et al., 2009a; Serafim, 1979), chemical oxidation (Abdelwahab et al., 2009), and biological techniques (Jou and Huang, 2003; Rahman and Al-Malack, 2006; Ma et al., 2009). New technologies such as membranes (Li et al., 2006a; Rahman and Al-Malack, 2006) and microwave-assisted catalytic wet air oxidation (Sun et al., 2008) have also been reported. Generally, these methods involve the transfer of contaminants from one medium to another; therefore, another step is required for the elimination of organic compounds. They are also characterised by low efficiencies and reaction rates, the generation of sludge and can operate only within a narrow pH range (Laoufi et al., 2008; Kuyukina et al., 2009). Another attractive technique is chemical oxidation. However, very low reaction rates (Huang and Shu, 1995) and the large amount of oxidants required when treating large quantities of waste (which are typical of industrial effluents) limit its application (Guo and Al-Dahhan, 2005). Advanced oxidation processes (AOPs), which are characterised by the generation of a hydroxyl radical ($^{\bullet}OH$), can potentially destroy a wide range of organic molecules. The $^{\bullet}OH$ has a high oxidation potential (estimated to be +2.8 V) relative to other oxidants. For ozone, H_2O_2, HOCl and chlorine, the oxidation potentials are 2.07, 1.78, 1.49, and 1.36, respectively (Al-Rasheed, 2005).

Among the numerous AOPs, heterogeneous photocatalytic degradation has been found to be a highly effective treatment technology (Li Puma and Yue, 2003). The choice of this technique was based on its great potential for the complete mineralisation of organic effluents, and the catalyst itself is non-toxic, cost effective and readily available (Laoufi et al., 2008; Gaya and Abdullah, 2008).

The main objectives of the paper are to: (i) discuss compositions and adverse effects of petroleum refinery effluents, (ii) highlight various processes employed in the pre-treating and the advanced treatment of PRE and (iii) focus on photocatalytic degradation by discussing the process principles, its applicability for treating typical organic pollutants found in PRE and by analysing existing works on PRE treatment using this process.

2. Petroleum industry

2.1. *Refinery configuration*

There are numerous possible refinery configurations, and each is designed to achieve the specific target of transforming crude oil into useful products such as dual-purpose kerosene, gasoline and petrochemical feed stock. Al Zarooni and Elshorbagy (2006) classified refineries into either a hydro-skimming unit comprised of three sub-units (a crude distillation unit, which fractionates crude oil into various components, a desulphurising unit, which reduces the sulphur content of some fractions such as kerosene and naphtha and a reforming unit for producing reformate) or a complex unit, which incorporates an additional catalytic cracking unit into the hydro-skimming refinery. Wake (2005) presented a broader categorisation, in which refineries were classified into four units. Petrochemical plants are sometimes incorporated within the refinery complex. Therefore, each PRE is a function of the number of units and the configuration of the refinery, which results in a lack of uniformity of the composition of the discharged effluent.

Regardless of configuration, the final waste stream generated is the contribution of the units involved with crude oil processing, e.g., hydro-skimming, hydro-skimmer flare, hydro-cracking, hydro-cracker flare, sourwater, condensate, condensate flare and the desalter. Other units not directly

Table 1 – Minimum standard discharge limits for refinery effluents.

pH[a]	Composition (mg/L)								Ref.
	COD	BOD	DOC	O&G	SS	Ammonia	Phenols	Sulphides	
6–9	100	10-15	–	10	70	15	–	–	Ma et al. (2009)
–	100	40	–	–	–	–	–	–	Hami et al. (2007)
6.7	200	–	20	23	–	70	3.7	–	Santos et al. (2006)
6-9	150	30	–	10	30	–	–	1.0	Environmental Health Safety Guidelines (2009)

[a] Dimensionless.

involved with processing, e.g., sanitary, crude tank and laboratory water, also contribute significantly to the total volume of the effluent (Al Zarooni and Elshorbagy, 2006).

2.2. Adverse effects of effluents

PRE are priority pollutants due to their high polycyclic aromatics contents, which are toxic and tend to be more persistent in the environment (Mrayyana and Battikhi, 2005; Wake, 2005). They encompass a wide range of contaminants at varied concentrations that are generally harmful. Decreased productivity of algae (a very important link in the food chain) observed for PRE-receiving water bodies have been attributed to such effects (El-Naas et al., 2009b; Pardeshi and Patil, 2008).

The minimum amount of dissolved oxygen necessary for normal life in an aquatic environment is about 2 mg/L (Attiogbe et al., 2007), and the discharge of high organic matter containing waste waters into water bodies results in the excess consumption of oxygen by the bacteria. This is in an attempt to oxidise the effluent, thus depleting oxygen from the water faster than it dissolves back into the water from the air (Attiogbe et al., 2007). This problem leads to the inadequate maintenance of higher life forms. In addition, oxygen availability is important because the end products of chemical and biochemical reactions in anaerobic systems often produce aesthetically displeasing colours, tastes and odours in water (Attiogbe et al., 2007).

Oil and grease are sticky in nature; they tend to aggregate, clogging drain pipes and sewer lines, causing unpleasant odours and corroding sewer lines under anaerobic conditions (Chen et al., 1999; Xu and Zhu, 2004). They also interfere with unit operations in municipal wastewater treatment plants because they float as a layer on top of the water. They also stick onto pipes and walls consequently blocking strainers and filters (Xu and Zhu, 2004).

Phenolic compounds pose a significant threat to the environment due to their extreme toxicity (Kavitha and Palanivelu, 2004), stability, bioaccumulation and ability to remain in the environment for long periods. They generally are carcinogenic, causing considerable damage and threaten the eco-system in water bodies along with human health (Abdelwahab et al., 2009; Lathasree et al., 2004; Pardeshi and Patil, 2008; Yang et al., 2008).

The nitrogen and sulphur components of the effluent are highly toxic and are represented in the form of ammonia and hydrogen sulphide (H_2S), respectively (Altas and Büyükgüngör, 2008). In aqueous form, H_2S exists in equilibrium with bisulphide (HS^-) and sulphide (S^{2-}), and the latter sulphide is the most reduced form (Altas and Büyükgüngör, 2008). Sulphide has a high oxygen demand of 2 mol O_2/L mol S^{2-} thus contributing significantly to oxygen depletion (Poulton et al., 2002). This results in mass fish mortality when the threshold limit exceeds 0.5 mg/L for freshwater or saltwater fish (Altas and Büyükgüngör, 2008). The degradation of water quality through PRE discharges and the quest for a cleaner environment caused by the increased awareness of the hazardous composition of PRE has resulted in various environmental protection agencies setting maximum limits of discharge for each component of the waste (Table 1).

3. Treatment techniques

There are two basic treatment stages. The first stage consists of mechanical and physicochemical treatments followed by the advanced treatment of the pre-treated primary effluent (see Fig. 1).

3.1. Pre-treatment step

The primary treatment step is essential as it allows for the efficient and prolonged use of the secondary treatment unit. Here, the heterogeneous components of the effluent, i.e., suspended solids (SS), immiscible liquids, solid particles and suspended substances (colloids or dispersions), are reduced significantly (Renault et al., 2009). This is achieved mechanically by gravity in API separators or separation tanks. Without the primary treatment, the presence of salts and sulphide in excess of 20 mg/L can strongly inhibit subsequent biological operation (Demirci et al., 1997; Altas and Büyükgüngör, 2008). Colloids and dispersion also hinder or damage equipment during the preceding stage (Renault et al., 2009).

The mechanical step is followed by the physiochemical step, in which heavy metal concentration is decreased and small-sized suspended solids are further reduced by agglomeration into large-sized particles to ease removal by filtration, sedimentation or floatation (El-Naas et al., 2009b).

3.2. Advanced treatment

The objective of this stage is to reduce the effluent contamination level to allowable limits for discharge into water bodies. Several techniques that are used as advance treatment methods are now briefly discussed.

The most widely applied technique is bioremediation. Although biological systems are capable of removing many of the dissolved organic carbons, recalcitrant components are not adequately eliminated. Petroleum effluents contain a high number of refractory compounds (Chavan and Mukherji, 2008); therefore, completely degrading them through biological means proves difficult. This is supported by higher COD

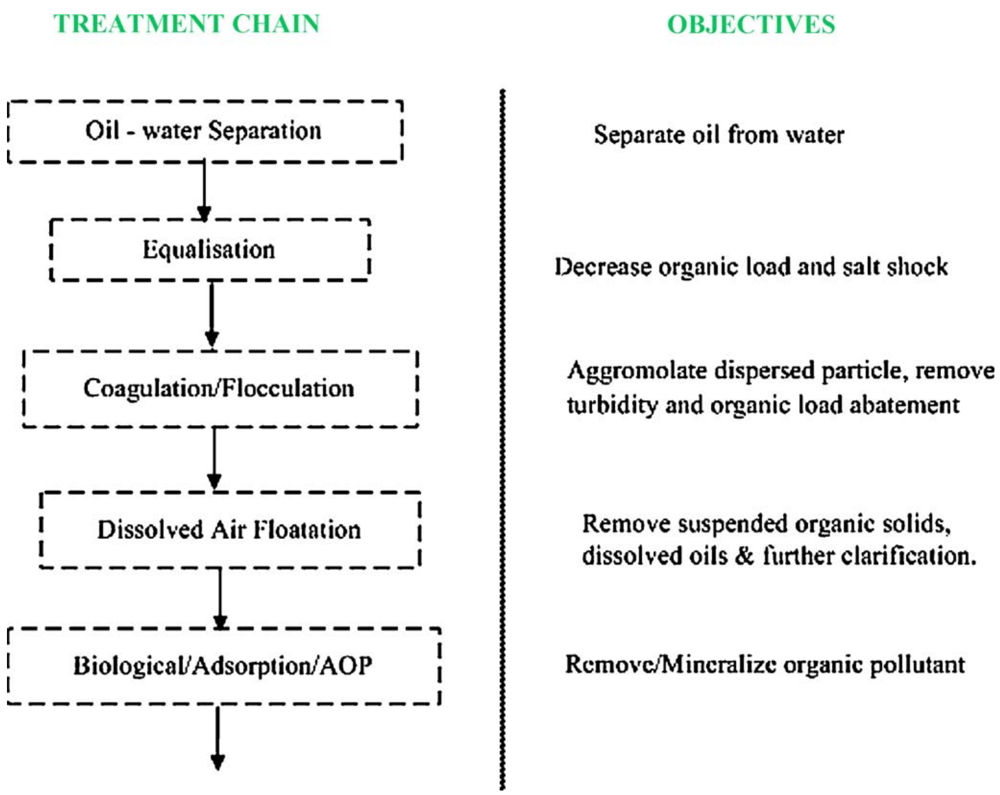

Fig. 1 – Schematic diagram of generic sequence for treating petroleum refinery effluent.

values observed in some treated effluents (Fratila-Apachitei et al., 2001). The remaining COD of treated effluents reflects the non-biodegradable components (Shokrollahzadeh et al., 2008).

These obstacles are addressed by inculcating and introducing indigenous, allochthonous or genetically modified organisms into biological systems (Ma et al., 2009). A novel investigation of an activated sludge system was conducted by Shokrollahzadeh et al. (2008) with the aim of addressing the system's inability to degrade a wide range of recalcitrant contaminants. An important result of the research was the successful isolation of 67 aerobic bacterial species that could be used in most types of bioremediation due to their excellent diverse catabolic activity. This approach was also adopted by Zhao et al. (2007), who used it to successfully degrade PRE.

The major drawbacks of the bioaugmentation process include the uncertainty of reproducibility at a full scale due to the dependence of the process on many variables (e.g., the chemical properties and concentration of the pollutants and the activity and survival of the consortia inoculated). These problems were remedied in a recent work by Ma et al. (2009), in which they upgraded the system to a full-scale oxidation system and obtained a 10-day adaptation time edge over the biological system.

Fluidised bioreactors (FBR) have been shown to be more efficient than conventional biological methods, with the potential to better degrade toxic pollutants, resulting in higher biomass concentrations and mass transfer. Despite these merits, organic degradation has proven to be low as was evident from the work by Ochieng et al. (2003) in a fluidised system, in which only 34% degradation was recorded in the presence of an available surface area of 2.13 m^2/kg (which is sufficient for microorganism attachment sites). These results agree with an earlier work by Holubar et al. (2000), in which 35.4% COD reduction was reported.

To enhance biodegradability, bacterial activity is increased through immobilisation on an inert support in fixed bed reactors. This method has shown improved COD removal with lower biomass loss at a lower HRT (Satyawali and Balakrishnan, 2008). This configuration has also been found to have a relatively higher tolerance to toxic and organic shock loads.

Numerous works on adsorption have been undertaken; however, a recent work by El-Naas et al. (2009a) attained 53% COD reduction at 60 °C, whereas at the ambient temperature only 30% was attained. Improved treatment through adsorption could be obtained by coupling the activated sludge with an addition of sorbent to form a biologically activated carbon system (BAC) unit. Although this combination results in a better reduction of the COD than a separate column, its cost is higher (Serafim, 1979). This is due to an increase in frequency of regeneration because more carbon loading is expected.

Membrane degradation of PRE in a cross-flow membrane system was reported by Rahman and Al-Malack (2006); their work recorded a 93% reduction in COD within an HRT of 17–22 h. However, for large volumes of effluent, it has been established that the use of a membrane is unsuitable. Microwave catalytic wet air oxidation (MW-CWAO) is another advanced treatment method. A recent work by Sun et al. (2008) addressed several of the process drawbacks by employing milder operation pressure and temperature (150 °C) versus conventional temperatures of 180–315 °C and pressures of 2–15 MPa. Although over 90% decrease in COD was recorded, a temperature of 150 °C is not favourable due to the high energy cost. Freezing was conducted by Gao et al. (2009) and Jean et al. (1999) as a PRE treatment approach; however, achieving the required temperatures (−10 and −25 °C) not only consumed a large amount of energy but also required longer treatment times (24 and 7.5 h). This method is not viable as the freezing

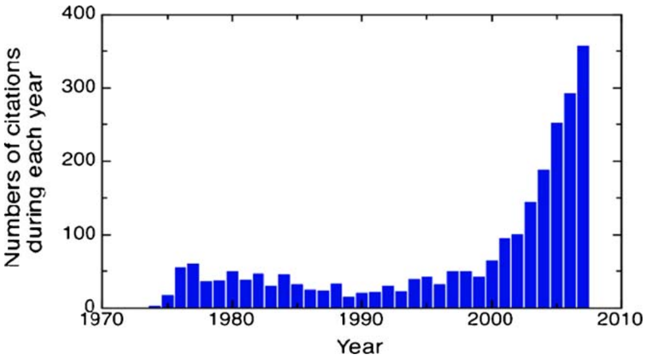

Fig. 2 – Yearly citations in research articles of the pioneer work on photocatalysis by Fujishima and Honda (1972) and Fujishima et al. (2008).

conditions required are practical only in regions where natural freezing conditions are prevalent.

4. Photocatalytic degradation

4.1. *Principles*

Heterogeneous photocatalytic degradation is a well-researched and established advanced oxidation process (AOP) used for wastewater treatment. Several excellent reviews have been written on the method (Akpan and Hameed, 2009; Fujishima et al., 2008; Rajeshwar et al., 2008), and the process continues to receive attention due to its potential for destroying a wide range of organic chemical substrates. This is evident from the large number of citations, especially during the last decade (Fig. 2), of the pioneering work of Fujishima and Honda (1972).

An advantage of this technique over other AOPs, such as homogeneous photo-Fenton, UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3, is complete mineralisation (Rajeshwar et al., 2008). The process also produces no sludge (Akpan and Hameed, 2009), has faster reaction rates, low cost (Wang et al., 1999) and operates well at ambient temperature and pressure conditions (Lin, 2005). Generally, UV/O_3 and UV/H_2O_2 are uneconomical as the process consumes large amounts of oxidant and has a high running cost (Kavitha and Palanivelu, 2004). On the other hand, the hazards associated with ozone utilisation (being an unstable gas) limit its application as the gas must be generated and used on-site. This is immediately coupled with the need for an ozone–water contacting device to transfer the ozone into its liquid phase (Huang and Shu, 1995).

4.2. *Parameters affecting the process*

As with most processing techniques, several variables affect the performance of photocatalytic degradation. However, a detailed analysis of specific effects on PRE treatment cannot be presented due to the lack of investigation on the variables. Nevertheless, this study considers the effects of typical organic compounds found in PRE (Table 2).

4.2.1. *Temperature effect*

The effect of this parameter is insignificant because photonic activation of the process occurs at a temperature range of 20–80 °C (Herrmann, 1999). The process' true activation energy is zero, and it has a very small apparent activation energy (AAE); therefore, no heating is required. This is supported by an AAE of 5.4 kJ/mol reported by Hong et al. (2001) for the degradation of phenol, which clearly indicates the functionality of the process at ambient temperatures. In the work of Chan et al. (2003), the photocatalytic degradation of benzoic acid was compared at room and elevated temperatures. Reactions at higher temperatures yielded relatively lower TOC removal than those occurring at room temperature. This is in agreement with work of Fox and Dulay (1996), who asserted that any increase in temperature for photocatalytic reactions is insignificant. Twesme et al. (2006) showed that degradation at an ambient temperature of 35 °C performed best for the degradation of propane and isobutene. They noted that a temperature increase from 70 °C to 100 °C had no significant effect on the mineralisation process, and they obtained a decrease in the mineralisation of n-butane at 100 °C. A decrease in mineralisation at high temperatures was attributed to a decrease in the DO levels of the effluent, the enhancement of charge carrier recombination and the desorption of adsorbed species (Chan et al., 2003; Gaya and Abdullah, 2008).

4.2.2. *Catalyst concentration*

In photocatalytic degradation, a linear relationship exists between the mass of the catalyst and the initial rates of reaction regardless of the catalyst configuration (Herrmann, 1999). Generally, an increase in catalyst concentration results in a very rapid increase in degradation, which conforms to a heterogeneous regime (Akpan and Hameed, 2009). A similar observation was made by Jain and Shrivastava (2008) in the case of cyanosine degradation, who investigated this effect on TiO_2 loading between 0.01 and 0.08 g/L. Higher catalyst concentrations result in an increase of the number of active sites available for adsorption. However, an increase of the catalyst concentration beyond a certain limit would not result in any significant change in the efficiency of degradation (Al-Sayyed et al., 1991; Alhakimi et al., 2003). This occurs when the maximum limit of photons absorption is reached within the reactor. Many authors have observed a decrease in organic removal efficiency with an increase in catalyst concentration beyond a certain limit (Wang et al., 1999; Kabir et al., 2006). Other factors contributing to this decrease are the blocking of light penetration and the scattering of the light (Gaya and Abdullah, 2008). This, in turn, results in a reduction of the available active sites and promotes the formation of an electron hole. For a catalyst in suspension, agglomeration may occur at higher concentrations, which reduces the available active sites along with a resulting decrease in efficiency (Huang and Shu, 1995). In packed bed systems, the optimum catalyst loading depends on the size of the packing material. The work of Dijkstra et al. (2001) further supports this as their formic acid degradation, which was done under the same experimental conditions but with varied packing sizes of 1.3 and 2 mm, gave an optimum catalyst loading of 0.2 and 0.46 g, respectively. Other figures reported by various researchers are presented in Table 3.

4.2.3. *Substrate concentration*

Process efficiency is greatly influenced by the initial COD concentrations of the effluent. This is demonstrated in the case of the photoelectrocatalytic degradation of produced water by Li et al. (2006a,b). They observed an increase in COD removal at concentrations of 316.9 mg/L and a decrease in COD removal at twofold concentrations (645.0 mg/L). A similar trend was observed when photon absorption was increased by decreasing the initial concentration of furfural solution (Faramarzpour et al., 2009), which led to higher catalyst acti-

Table 2 – Typical organic, inorganic and oily effluents found in PRE mineralised/degraded by photocatalytic degradation.

Pollutant type	Ref.	Parameters investigated	Results of degradation and comments
Oily and greasy effluents	Adams et al. (2008)	COD	85% COD reduction in 10 min, eliminated need for aeration through mechanical mixing
	Grzechulska et al. (2000)	COD and oil content	Degraded oil bilge wastewater permeates in 2 h by modification of catalyst activity. Report failed to present measured COD, and concentration of oil used was already below discharge limit
	Alhakimi et al. (2003)	COD	Complete degradation of oily wastewater in 5 h
	Jain and Shrivastava (2008)	COD	82.5% reduction in COD within 40 min irradiation for high initial COD of 1345 mg/L
Crude oil water soluble fractions	Ziolli and Jardim (2002)	Mineralisation	Complete mineralisation within 24 h
Oil field produced water	Li et al. (2006a)	COD	Reduction in COD level of 80%, 88.9% and 93.0% COD at 30, 60 and 120 min, respectively
Industrial wastewater	Chen et al. (2004)	COD, BOD	Improved biodegradability within 30 min; reduced COD and BOD_5 by 93.9 and 88.7%, respectively
	Herrmann (1999)	COD	COD reduction to 95% in 4 h after 1 h adsorption in dark environment
	Wang et al. (1999)	DOC	Decreased DOC from 30% to 75% by aerating the system
	Al-Bastaki (2004)	Concentration	Removal of 99.3% benzene within 15 min
	Silva et al. (2007)	COD, TOC, phenol	In 2 h, 97.5%, 98.9% and 97.1% reduction in COD, phenol and TOC, respectively, for synthetic wastewater; OMW values were 82.1% and 98.6% for TOC and total phenol, respectively
Oxalic acid	Kobayakawa et al. (1998)	Mineralisation	Complete degradation of 1 mM oxalic acid within 18 min by double-sided irradiation versus 70% from one-sided irradiation
Benzoic acid	Chan et al. (2003)	TOC	Scaled bench scale reactor to pilot plant. Achieved complete degradation in 3 h. Added 10 mL H_2O_2 and enhanced removal from 30% to 83% at lower temperatures
Dodecane, Toluene	Minero et al. (1997)	Mineralisation	Salinity does not affect process
Furfural	Faramarzpour et al. (2009)	Mineralisation	More than 95% degradation within 2 h
Trichloroethylene	Yamazaki et al. (2001)	Mineralisation	Complete degradation within 2 h
Phenols	Kabir et al. (2006)	Mineralisation	Mineralised about 98% of phenol within 2.5 h of irradiation and use of 20% H_2O_2
	Laoufi et al. (2008)	Mineralisation	99% mineralisation within 4 h
	Hong et al. (2001)	Mineralisation	Complete degradation in 90 min
Sulphides	Habibi and Vosooghian (2005)	Mineralisation	Average complete mineralisation of four organic sulphide compounds within 3 h

Table 3 – Catalyst loading and corresponding optimum values.

Ref.	Catalyst loading (g/L)	Optimum loading (g/L)
Li et al. (2006a)	0.5–2.5	2.0
Jain and Shrivastava (2008)	0.01–0.08[a]	–
Silva et al. (2007)	0–1.5	0.75
Kabir et al. (2006)	0.21–2.14	1.61
Laoufi et al. (2008)	0.1–1.0	0.2
Hong et al. (2001)	1.0–4.0	2.0
Dijkstra et al. (2001)	0–10 kg/m^3 and 0–3.6 g/m^2	–
Habibi and Vosooghian (2005)	0–60[a]	30.0[a]

[a] mg/L.

vation with a subsequent improvement of photocatalytic degradation. Silva et al. (2007) also observed a decrease in processing time; they obtained complete phenol degradation at a concentration of 163 mg/L in 15 min versus 60 min for 650 mg/L. Higher concentrations of a pollutant can enhance or retard the process (Li et al., 2006a) if it is not optimised. At higher concentrations, the number of collisions between organic pollutants and the catalyst is high, which promotes degradation. However, at a certain limit, when the surface is saturated through the adsorption of a pollutant, the reaction between the reacting molecules and the photo-induced positive holes or $^{\bullet}OH$ is inhibited (Li et al., 2006b). This result strongly suggests the need to optimise these parameters.

4.2.4. *Initial pH*

This parameter has a significant effect on the organic pollutant rate of the degradation process (Alhakimi et al., 2003). It is a complex phenomenon because the surface of the catalyst can assume different ionisation states (Akpan and Hameed, 2009) and affect the extent of adsorption of the substrate on the catalyst surface (Silva et al., 2007). The effluent pH affects the surface of titania by protonation or deprotonation according to Eqs. (1) and (2) (Habibi and Vosooghian, 2005).

$$TiOH + H^{+} \rightarrow TiOH_2{}^{+} \quad (1)$$

$$TiOH + OH^{-} \rightarrow TiO^{-} + H_2O \quad (2)$$

Yang et al. (2007) reported a similar effect of effluent pH on the surface of TiO_2, and they proposed the formation of three different species to account for variations of the behaviour of the catalyst with pH. The species, namely TiOH, $TiOH_2{}^{+}$ and TiO^{-} (Eqs. (3) and (4)) are formed on the amphoteric surface due to acid–base equilibria depending on the solution pH and the point-of-zero charge (pHpzc) of the catalyst.

$$TiOH_2{}^{+} \rightarrow TiOH + H^{+} \quad (3)$$

$$TiOH \rightarrow TiO^{-} + H \quad (4)$$

Positive holes are the predominant oxidation species at low pH while $^{\bullet}OH$ are abundant in wastewater at high and neutral pH (Akpan and Hameed, 2009). This implies that degradation would be enhanced in alkaline wastewater with a positively charged surface because coulombic repulsion with hydroxide anions would not be present. An acidic medium can also favour organic degradation as shown by the degradation of acid brown 14 (Sakthivel et al., 2002). Higher degradation was obtained in an acidic environment due to strong adsorption from electrostatic attraction between the cationic titania and dianionic dye. However, in the alkaline medium, the titania acquired a negative charge with attendant repulsion between the catalyst and organic dye, thus retarding the adsorption rate and resulting in lower efficiency. Nonetheless, the catalyst pH can be manipulated during preparation.

The iso-electric point of TiO_2 ranges between pH 4 and 6 (Li et al., 2006b), and this accounts for the presence of $TiOH_2{}^{+}$ and TiOH as the predominant species in an acidic effluent with a positively charged catalyst surface (Yang et al., 2007). For alkaline effluents the surface becomes negatively charged. It has been shown that the degradation of the same category of organic compound can be favoured by different pH values; this was shown to be the case for sulphide degradation (Table 2) by Habibi and Vosooghian (2005), where methyl phenyl sulphide (MPS) degradation was favoured by an alkaline medium, and methyl benzimidazoyl sulphide (MBS), propyl benzimidazoyl sulphide (PBS) and 3-propenylbenzimidazoyl sulphide (3-PBS) were better degraded at a neutral pH.

4.2.5. *Radiation intensity*

In organic degradation, a non-linear relationship exists between strong light intensity and decomposition. Kobayakawa et al. (1998) irradiated both sides of a reactor for the decomposition of oxalic acid, but the result was not double that obtained from one-side irradiation. Generally, an increase in decomposition is associated with an increase in light intensity due to an increase in the photon flux of electrons in the conduction band (Vohra and Tanaka, 2002). This photon flux enhances photocatalytic degradation by causing favourable collusion chances between photons and activatable centres (Wang et al., 1999), thereby suppressing electron hole recombination. This phenomenon is corroborated by the works of Silva et al. (2007), who observed a steady decrease in degradation of phenol. Their work does not contradict that of Kobayakawa et al. (1998) as their range of investigation was limited by decreasing intensity from 400 W to 250 W and finally to 9 W. A broader study was carried out by Kobayakawa et al. (1998), who showed that, for moderate to high intensities, decomposition percentage increased with the square root of incident light. They also cited six other works in agreement with their study, and the range of these works covered both suspended and fixed catalysts.

4.2.6. *Oxidants concentration*

The mineralisation efficiency of a photocatalytic process is enhanced by preventing charge recombination. This can be achieved by the introduction of any of several electron acceptors (H_2O_2, HO_2, O_3, $S_2O_8{}^{2-}$). Yang (2008) introduced a detailed mechanism of the dissociation of these electron acceptors into highly reactive radicals during electron acceptance.

Table 4 – Photocatalytic degradation of petroleum refinery effluent.

Ref.	Parameters investigated	Highlights
Saien and Nejati (2007)	COD	Over 90% and 61% COD reduction obtained in 4 and 2 h, respectively
Coelho et al. (2006)	COD	Attained low COD reduction (21% COD), however, reaction time was 1 h and oxidant dosage was not optimised
Santos et al. (2006)	DOC, O&G, ammonia and phenols	Use of H_2O_2 was found to have negligible effect. Photocatalytic activity decreased as pH value tends to neutrality
Stepnowski et al. (2002)	TPH, DCE, DCM and tBME	Achieved total degradation of TPH in 24 h. Exposed same sample to unaided degradation and obtained 31% and 20% for DCE and DCM after 8 days while during same period of study DCM and tBME were not changed

Lastly, a decrease in flow rate for continuous systems has been shown to result in an increase of degradation due to an increase in resident time, thereby effectively enhancing reactant and catalyst contact (Twesme et al., 2006). Different degradations can be found using any of the oxidants mentioned above; the statement was validated by the degradation of trichloroethylene by Yamazaki et al. (2001). They observed that the addition of $S_2O_8^{2-}$ resulted in a fivefold increase of efficiency compared to a reaction without oxidant addition, and a reduction in degradation was observed with the addition of H_2O_2. These findings clearly indicate that, for the efficient performance of photocatalytic degradation, variable optimisation is essential.

4.3. *Refinery wastewater*

Basically, PRE are complex matrices of organic pollutants, and it is well established that photocatalytic degradation can completely mineralise oily and hydrocarbon-rich waste waters. Furthermore, all of the different types of organic substrate typically found in PRE (Table 2) are also mineralised; therefore, by default, PRE can be effectively treated.

Stepnowski et al. (2002) investigated the degradation of pre-treated PRE in a batch reactor and obtained a total TPH reduction within 24 h by the addition of 11.76 mM H_2O_2. In the same study, an unaided biodegradation of the sample was undertaken, and only 69% was degraded after eight days. It should be noted that the remaining undegraded TPH were composed of the fuel additives dichloroethane (DCE), dichloromethane (DCM) and *t*-butyl methyl ether (tBME), which are carcinogenic (Squillance et al., 1996). A similarly long degradation period was reported by Knap and Williams (1982), who obtained 70% hydrocarbon degradation after 40 days, whereas Saien and Nejati (2007) reported aided biodegradation achieving 77% in 18 h.

All of the operating parameters affecting organic contaminant degradation (discussed in Section 4.2) apply to PRE degradation. The use of H_2O_2 as an oxidant has been investigated in all of the works discussed in this paper except for Saien and Nejati (2007), and an increase in photocatalytic activity was observed when it was used. However, Santos et al. (2006) reported that H_2O_2 did not contribute significantly to the degradation. In their work, higher removal efficiencies of 93%, 63% and over 50% for phenol, dissolved organic carbon (DOC) and oil and grease, respectively, were achieved within 1 h. This might be due to the use of previously treated PRE from a biological unit, an indication that the contamination level was low. Table 4 shows that the highest level of degradation was achieved in the work of Saien and Nejati (2007), in which they obtained 90% COD reduction using a pre-treated effluent. This high COD removal was attained at a relatively low catalyst concentration of 100 mg/L (in comparison with 200 mg/L reported by Coelho et al. (2006)) and occurred within 4 h.

Globally, PRE treatment is based on a multiple and sequential approach to decontaminating a single stream generated from the merger of several streams. Contributing streams in some refineries total up to 15 streams (Fratila-Apachitei et al., 2001). Each stream's volumetric and toxic load differs (Al Zarooni and Elshorbagy, 2006), and the overall treatment process is basically an end-of-pipe and non-distributive process. To achieve a reduction in the amount of water consumed in petroleum refining plants, Bagajewicz (2000) proposed a roadmap for the improved processing of effluent by recycling certain specific streams. These new design procedures were based on decentralising the treatment by introducing series/parallel wastewater treatment rather than merging the streams. One of these streams is the sourwater stream (SWS), which is produced by injecting some units with steam to reduce hydrocarbon partial vapour pressure. The procedure enables petroleum refining operations to be undertaken at a less extreme temperature (Coelho et al., 2006).

Coelho et al. (2006) considered SWS for segregation and treatment due to its complex chemical composition, which consists of emulsified oil, phenols, sulphides, mercaptans, ammonia, cyanides and other micropollutants. The volumetric contribution of this stream to the total effluent discharged is usually the highest (Al Zarooni and Elshorbagy, 2006). Table 5 shows that the average sulphide concentration in the effluent is about 20 mg/L, but the contribution from SWS can sometimes reach 150 mg/L (Altas and Büyükgüngör, 2008); this could explain the high sulphide concentrations reported by El-Naas et al. (2009b). Given the above data, Coelho et al. (2006) degraded an SWS in a photocatalytic batch reactor and reported a 21% reduction in DOC values within 1 h of irradiation time at a catalyst loading of 200 mg/L.

This result is low compared to that found by Saien and Nejati (2007), who obtained 90% COD reduction with half the catalyst concentration employed by Coelho et al. (2006). The operating conditions used by Stepnowski et al. (2002) are more promising, as the effluent had a higher organic load (1533.9 ± 107.0 mg/L TPH). However, in the same study, an 83% reduction in DOC using the photo-Fenton method was obtained. A relatively higher DOC reduction was obtained by the UV/H_2O_2 system than the photocatalytic system. These results suggest that the comparison was not adequate. Reac-

Table 5 – Typical compositions of some petroleum refinery effluents.

pH[a]	Composition (mg/L)								Ref.
	COD	BOD	DOC	O&G	SS	Ammonia	Phenols	Sulphides	
7–9	300–600	150–360	–	≤50	≤150	15	–	–	Ma et al. (2009)
8.0	80–120	40.25	–	NR	22.8	–	13	–	Abdelwahab et al. (2009)
6.6	596	–	–	–	120	–	–	887	El-Naas et al. (2009a)
8.44	216	–	–	–	–	–	–	22	Altas and Büyükgüngör (2008)
6.5–7.5	170–180	–	–	–	420–650	–	–	–	Saien and Nejati (2007)
NR	300–800	150–350	–	3000	100	–	20–200	–	Al Zarooni and Elshorbagy (2006)
6.7	200	–	20	23	–	70	3.7	–	Santos et al. (2006)
8.0–8.2	850–1020	570	300–440	12.7	–	5.1–21.1	98–128	15–23	Coelho et al. (2006)
–	68–220	0.2–1.2	10.4–31.3	1.1–3.5	–	0.21–21.23	0.85–3.75	–	Rahman and Al-Malack (2006)
8.1–8.9	510–911.9	–	–	–	–	–	30–30.6	–	Jou and Huang (2003)
6.5	800	–	350	3000	100	–	8	17	Demirci et al. (1997)
10	80.8	8.0	–	47.5	–	2.3	–	–	Ojuola and Onuoha (1987)
NR	658–710.5	–	185	45	NR	22	30	10	Serafim (1979)

[a] Dimensionless.

tions are faster and more efficient in photocatalytic systems than UV/H_2O_2 because photocatalysis is much more oxidative (Santos et al., 2006). The low degradation obtained by Coelho et al. (2006) might be due to the adverse effect of excess H_2O_2 on the reaction as described by Li et al. (2006a), who stated that H_2O_2 consumes generated $^{\bullet}OH$ if the optimal dosage is not computed and employed. One form of this effect can be seen through short-circulating the semiconductor microelectrode (Akpan and Hameed, 2009) via Eqs. (5) and (6):

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2 \tag{5}$$

$$HO_2 + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{6}$$

Therefore, it is imperative to determine the stoichiometric amount of hydrogen peroxide sufficient for complete mineralisation (Gernjak et al., 2003). This analysis was not presented in their work. It should be noted that all results presented for the photocatalytic treatment of PRE were not optimised. Thus, by implication, optimising the process would result in a shorter reaction time, the maximal utilisation of the catalyst and higher degradation efficiencies.

5. Conclusions

Petroleum refinery effluents (PRE) are hazardous compounds containing waste. The discharge of these waste waters into the environment adversely affects the ecosystem. An increasing global energy demand requires greater exploration and exploitation of the raw material, crude oil, that is responsible for these pollutants. A consequence of processing crude oil in petroleum refineries is the generation of these toxic effluents, which is estimated at 33.6 million barrels per day worldwide.

The treatment of PRE has undergone changes in technological approaches both at the pre-treatment and at the advanced stages. The physical separation of oil, colloids and suspended solids remains the preferred pre-treatment method due to its efficiency in separating heavier fractions of the waste. Many technologies are used for the advanced treatment stage of the primary effluent; however, each possesses several drawbacks.

Some recalcitrant and persistent compounds are not adequately eliminated by the biological method, which is the traditional approach. This is due to the high number of refractory components in PRE. Many advances have been made to improve performance ranging from bioaugmentation to fluidised bioreactors. However, the problems of high sludge generation, low tolerance to toxic load and organic shock coupled with a slow degradation rate persist. Other methods are either separative, require extreme temperature and pressure operating conditions or cannot handle large volumes of refinery waste waters effectively.

The poor performance of these processes necessitates the search for more viable alternatives. An attractive wastewater treatment technique is photocatalytic degradation; a process that potentially mineralises all of the organic and inorganic components typically found in the refinery effluent to environmentally benign by-products. It is also an efficient and cost-effective technique that is suitable for PRE treatment at the advanced stage. However, available information in the literature is scarce regarding the process for the treatment of PRE, and this greatly limits the industrial application of the process in refinery treatment plants. Although relatively high efficiencies for photocatalytic degradation have been achieved by a few reported works, optimising the process parameters would yield much better results.

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