

COD removal from petrochemical wastewater by UV/hydrogen peroxide, UV/persulfate and UV/percarbonate: biodegradability improvement and cost evaluation

Ali Akbar Babaei and Farshid Ghanbari

ABSTRACT

The petrochemical industry has been highly considered by environmentalists since it can affect the environment through the production of high strength wastewater. This study investigates chemical oxygen demand (COD) removal from petrochemical wastewater by ultra violet (UV)/oxidant systems with varying dosages of oxidants, initial pH values and reaction time. Hydrogen peroxide (H_2O_2), persulfate (PS) and percarbonate (PC) were used as oxidants. The results showed that pH = 3.0 was suitable for H_2O_2 and PC, while PS had the best performance at pH = 7.0. The presence of ferrous ions improved the removal efficiency, especially in the case of UV/PC. However, COD removal efficiencies of UV/PS and UV/ H_2O_2 were more effective than that of the UV/PC system. The biochemical oxygen demand (BOD)/COD ratio achieved >0.4 by UV/PS/ Fe^{2+} , UV/ H_2O_2 and UV/ H_2O_2/Fe^{2+} systems. Complete decolorization occurred for all the UV/oxidant systems after only 30 min reaction time. Besides the effective performances of PS and H_2O_2 in COD removal, PC was considered as an inexpensive oxidant. The order of total costs based on kg COD removed was: UV/PS/ Fe^{2+} > UV/PS > UV/ H_2O_2/Fe^{2+} > UV/ H_2O_2 > UV/PC/ Fe^{2+} > UV/PC. In conclusion, UV/ H_2O_2 displayed an effective, applicable and clean process for petrochemical wastewater treatment.

Key words | biodegradability improvement, percarbonate, persulfate, petrochemical wastewater, sulfate radical

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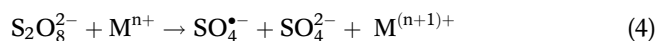
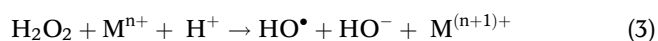
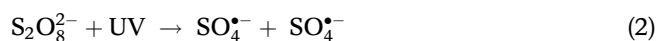
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INTRODUCTION

The petrochemical and oil industries are the most important industries in Iran. Despite the economic importance of the petrochemical industry, its environmental impacts are of concern. One of the main environmental issues of this industry is the production of vast amounts of wastewaters of various qualities. On the other hand, the quantity of petrochemical wastewater is also a critical concern since 0.4–1.6 L of wastewater is produced for each liter of processed oil (Ishak *et al.* 2012; Rubio-Clemente *et al.* 2015). The presence of various toxic compounds such as polycyclic aromatic hydrocarbon, benzene hydrocarbons, aniline, nitrobenzene and phenols require particular attention for the efficient treatment of this wastewater (Ma *et al.* 2009; Sponza & Gök 2010). There are many methods for treatment

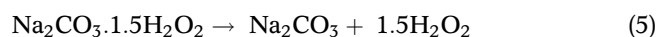
of petrochemical wastewater. Biological processes are the most common methods of petrochemical wastewater treatment, since these methods are inexpensive and environmentally friendly (Wu *et al.* 2015). However, these processes have limitations in the degradation of non-biodegradable compounds because some compounds of petrochemical wastewater are toxic and inhibit the growth and activity of microorganisms, and this increases when there is high salinity in the wastewater (Ghosh *et al.* 2010; Wu *et al.* 2015). Physico-chemical processes such as coagulation and adsorption can effectively remove organic compounds from wastewater. Nevertheless, these processes just transfer organic matter from liquid media to solid media and produce concentrated sludge that requires further

treatments (Khataee *et al.* 2009; Eslami *et al.* 2013). Membrane technology is an effective process for the separation of organic compounds from wastewater. Due to the possibility of fouling the membrane modules, the operational costs consequently increase (Zhao *et al.* 2006; Yeruva *et al.* 2015). Electrochemical processes have also been examined for petrochemical wastewater, but high electrical energy limits their application on a large scale (Yavuz *et al.* 2010). In recent decades, there has been notable interest in the application of oxidative processes for non-biodegradable wastewaters. Advanced oxidation processes (AOPs) have been defined based on the production of free radicals which are powerful and extremely reactive oxidant agents that can efficiently degrade organic pollutants (Pignatello *et al.* 2006). These radicals can be produced by various methods; the most conventional methods are the use of a chemical oxidant such as hydrogen peroxide. In recent years, persulfate (PS) has proven to be an alternative oxidant to produce free radicals for the degradation of organic pollutants (Hazime *et al.* 2014). These oxidants should be activated to produce free radicals. In order to activate the oxidants, ultra violet (UV) (Jaafarzadeh *et al.* 2015; Moradi *et al.* 2015), transitional metals (Ghanbari *et al.* 2014) and ultrasound (Hou *et al.* 2012) have been applied, which produce hydroxyl and sulfate radicals in the presence of H₂O₂ and S₂O₈²⁻, respectively.

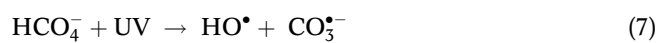


Hydroxyl radical and sulfate radical are strong oxidizing agents with $E^0 = 2.7 \text{ V}$ and $E^0 = 2.6\text{--}3.1 \text{ V}$, respectively (Buxton *et al.* 1988; Anipsitakis & Dionysiou 2003). Hydroxyl radical is a non-selective oxidant with a lifetime of 20 ns while sulfate radical is a selective oxidant with a longer lifetime (30–40 μs) (Ghanbari *et al.* 2014). Therefore, sulfate radical has the opportunity to react with the organic

compounds. Percarbonate (PC) has been recently considered as an alternative for hydrogen peroxide. Sodium percarbonate (Na₂CO₃·1.5H₂O₂) is a common source of PC, and is actually a hydrogen peroxide solid which is easy to transport and store. The sodium percarbonate is dissociated in water to hydrogen peroxide and sodium carbonate (Rivas *et al.* 2010; Miao *et al.* 2015):



In addition, there is a possibility of other reactions in solution when UV is irradiated. Hydrogen peroxide reacts with bicarbonate and consequently produces peroxymonocarbonate (Equation (6)); peroxymonocarbonate produces hydroxyl and carbonate radicals in the presence of UV (Equation (7)) (Rivas *et al.* 2010):



Several studies have used the application of UV/oxidant for degradation of pollutants. In recent years, an increasing concern in the UV/PS process for various contaminants has emerged and atenolol (Liu *et al.* 2013), various dyes (Yang *et al.* 2010), antipyrine (Tan *et al.* 2013), bisphenol A (Huang & Huang 2009) and surfactant (Saien *et al.* 2011) have been investigated by many researchers. However, a few surveys have been conducted on real wastewater treatment by UV/PS, and no study has been carried out on petrochemical wastewater as yet. Furthermore, the application of UV/PC has not been considered for real wastewater treatment.

The main objective of this work was the comparison of UV/hydrogen peroxide, UV/PS and UV/PC systems in chemical oxygen demand (COD) removal from real petrochemical wastewater. Moreover, decolorization of the petrochemical wastewater was also evaluated. The effects of the presence of ferrous ions in UV/oxidant systems were also assessed in terms of COD removal. Biodegradability improvement was evaluated by the biochemical oxygen demand (BOD)/COD ratio in different processes. Finally, the cost analysis of the processes based on kg COD removed was estimated as an economical aspect for application on a large scale.

MATERIALS AND METHODS

Wastewater sampling

The petrochemical wastewater was collected from a site in Mahshahr city located in Khozestan province, Iran. The collected samples were stored at a temperature of 4 °C in a refrigerator. The characteristics of petrochemical wastewater are summarized in Table 1.

Sulfuric acid (98%), sodium hydroxide, ferrous ammonium sulfate and hydrogen peroxide (30%w/w) were supplied by Merck Company (Darmstadt, Germany). Sodium percarbonate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$) as a source of PC was purchased from Sigma-Aldrich (St Louis, MO, USA). Sodium persulfate was provided from Fluka (Buchs, Switzerland). Silver sulfate and mercury sulfate were purchased from Sunchun Company (Seoul, South Korea). All sample solutions were prepared using deionized water (Karoon Ghatreh Inc., Ahvaz, Iran).

Experimental procedure

The photo-oxidation process was carried out in a batch reactor under room temperature. A cylindrical quartz reactor (6 cm diameter \times 16 cm height) was used for 300 mL of petrochemical wastewater. The cylindrical quartz reactor was surrounded by four lamps situated 90° apart. The distance between the lamps and photo-reactor was 3 cm. Irradiation was undertaken using four UV-C lamps (6 Watt, Philips) with maximum emission at a wavelength of 254 nm. In order to ensure safe operation, the reactor and the lamps were inserted in a wooden box to prevent the influx of extraneous UV light. Prior to photo-oxidation,

UV lamps warmed up for 10 min to reach a stable emission. The intensity of the UV-C light of the lamps was 7.15 mW/cm² at the center of the reactor. After introducing the samples to the reactor, the pH was adjusted by H₂SO₄ (1N) or NaOH (1N) then a certain amount of oxidant (hydrogen peroxide, PS and PC) was added to the sample while the solution was agitated with a magnetic stirrer to ensure complete mixing. Initial pH values and oxidant dosages ranged from 3 mM to 10 mM and 5 mM to 20 mM, respectively. Added amounts of pH adjusting agent and oxidant dosage were negligible in comparison with the total volume of treated wastewater. At regular time intervals, samples were withdrawn for COD analysis. The volume of total sampling was kept under 3% of the total solution volume. All experiments were conducted in triplicate and average values were used in the results, while standard deviations in all cases were lower than 3%. The photo-oxidation reactor is schematically represented in Figure 1. In the photo-oxidation process, the main costs are related to electrical energy consumption (EEC) and applied chemicals (oxidant dosage). EEC is calculated by Equation (8) (Arslan *et al.* 2000; Shu *et al.* 2013):

$$EEC = \frac{Pt1000}{V \times (COD_0 - COD_t)} \quad (8)$$

Table 1 | Characteristics of studied petrochemical wastewater

Parameters	Units	Values
COD	mg/L	950 ± 50
BOD ₅	mg/L	190 ± 10
Cl ⁻	mg/L	4550 ± 50
EC	mS/cm	11.25 ± 0.1
Color (absorbance at 400 nm)	cm ⁻¹	0.411 ± 0.003
pH	-	7.10 ± 0.04
TSS	mg/L	<100

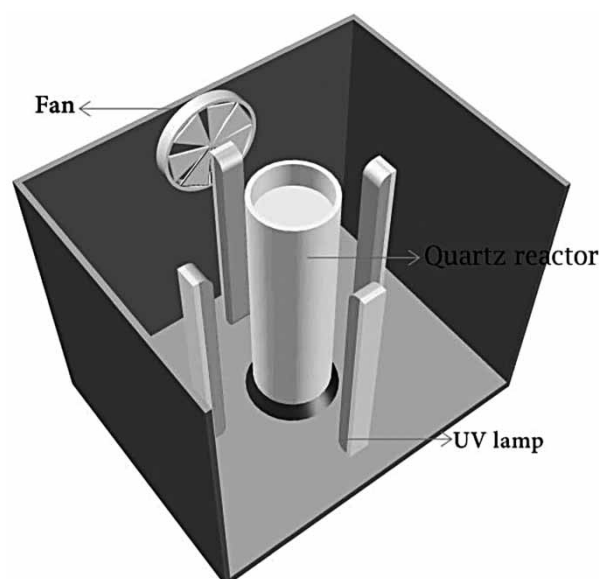


Figure 1 | The schematic representation of photo-oxidation reactor.

where P is the power of the UV lamp (kW), t is photolysis time (h), V is the reactor volume (L) and EEC is electrical energy consumption (kWh/kg_{COD removed}). The costs of chemicals (commercial) were calculated based on Iran's market in October 2015. The cost of electrical energy was considered according to industrial consumption, which was equal to 0.0147 US\$ per 1 kWh.

Analysis methods

COD values were measured by the open reflux method. Briefly, organic matters were oxidized by potassium dichromate under acidic conditions. The solution temperature was boosted to 150 °C for 2 h, then the residual potassium dichromate was titrated using ferrous ammonium sulfate. The chloride ion was determined by titration with silver nitrate (APHA 1999). The BOD₅ value was evaluated by determining oxygen consumption using titration with sodium thiosulfate after 5 days of incubation (the micro-organism culture was provided from the sludge of a municipal wastewater treatment plant). The color of the wastewater was measured by a UV-Vis spectrophotometer (Hach DR5000) at 400 nm as the wavelength of the maximum absorbance at the visible wavelength. A digital pH meter (Cyberscan 1500, Eutech) was utilized for measuring wastewater pH. Electrical conductivity was determined by an EC meter (Model 44600, Hach).

RESULTS AND DISCUSSION

Effect of pH on COD removal

The solution pH is one of the largest factors in chemical oxidation processes. The acidic condition (pH = 3.0), neutral condition (pH = 7.0) and alkali condition (pH = 10.0) were chosen for evaluating the effect of pH on COD removal in three processes. Figure 2(a) shows the effect of pH on COD removal in the UV/H₂O₂ system with 10 mM H₂O₂. As can be seen, acidic conditions provided further degradation of organic matters for UV/H₂O₂, since 52.6% of COD was removed at pH 3.0 compared to 38.9 and 26.3% for pH 7.0 and 10.0, respectively. This is attributed to the high oxidation power of HO[•] in an acidic pH. With

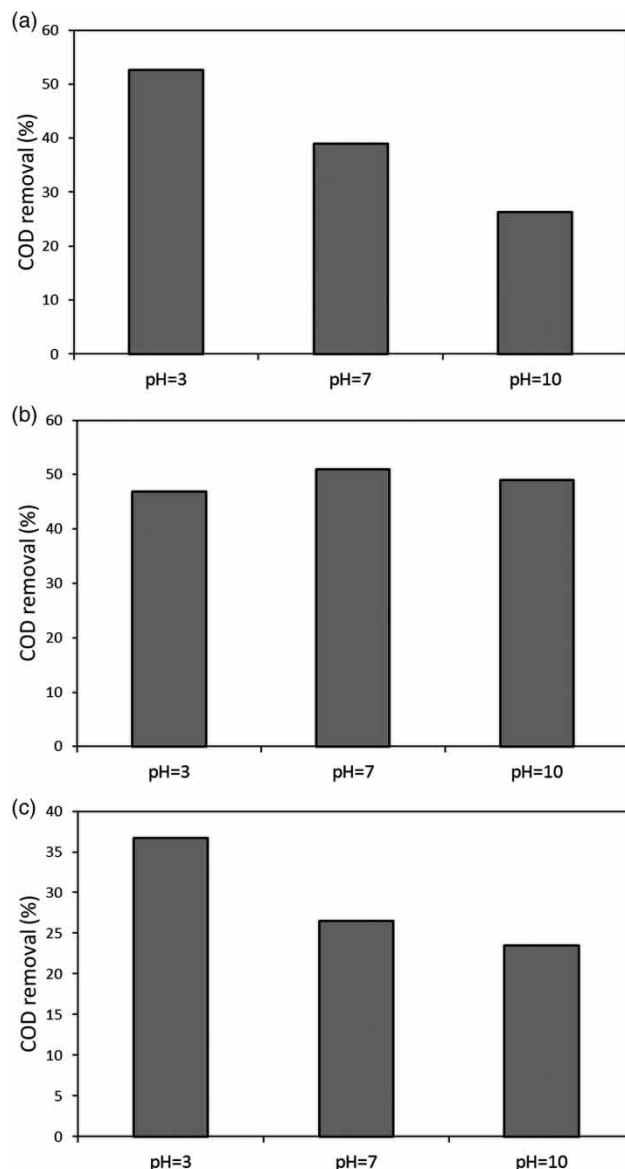


Figure 2 | The effect of pH on COD removal in UV/oxidants systems: (a) UV/H₂O₂ (H₂O₂ = 10 mM, time = 60 min), (b) UV/PS (PS = 10 mM, time = 60 min), (c) UV/PC (PC = 10 mM, time = 60 min).

an increase in pH, the oxidation power of HO[•] is decreased. In alkaline conditions, HO₂⁻ is the dominant form, and the molar extinction coefficient of HO₂⁻ on UV absorption is lower than that of H₂O₂ in the UV/H₂O₂ system (Tan *et al.* 2013).

Figure 2(b) displays the effect of pH on COD removal using UV/PS with 10 mM PS. In the UV/PS system, pH did not significantly influence COD removal from petrochemical wastewater. COD removal efficiencies were 47%,

51% and 49% for pH 3.0, 7.0 and 10.0, respectively. There was no significant difference in removal efficiencies with various pH values. In contrast to UV/H₂O₂, PS/UV has an acceptable performance in alkali conditions. This behavior is related to the generation of the hydroxyl radical, which results from the reaction of the sulfate radical with the hydroxide ion based on Equation (9). Hence, the hydroxyl radical can participate in the degradation of organic compounds in the UV/PS system (Saien *et al.* 2011; Ahmadi *et al.* 2015). Applying UV/PS, no pH adjustment was required regarding achieving the highest performance at pH 7.0 (natural solution pH) which is superior from an economical point of view:



Figure 2(c) displays the COD removal efficiencies at various pH values in the UV/PC system. As can be seen, an increase of pH reasonably reduced the COD removal efficiency. Maximum COD removal was observed at pH 3.0 with 36.7% removal efficiency. At an acidic pH, H₂O₂ is more stable than in alkali conditions since COD removal was 23.5% at pH 10.0. Moreover, the hydroperoxide anion increased at pH 10.0 and it scavenged the hydroxyl radical (Tan *et al.* 2013). The trend of COD removals at various pH values in UV/PC was similar to UV/H₂O₂. Hence, the subsequent experiments were carried out at pH 3.0 for UV/PC and UV/H₂O₂ while UV/PS was performed at pH 7.0.

The effect of oxidant dosage on COD removal

The effect of oxidant dosages on COD removal from petrochemical wastewater was tested by oxidant dosages of 5, 10, 15 and 20 mM at the optimized pH in the previous step.

Figure 3(a) depicts the effect of oxidant dosage on COD removal from petrochemical wastewater in the UV/H₂O₂ system. As seen, the COD removal rates significantly increased by increasing the H₂O₂ dosage and reached a maximum level at 15 mM H₂O₂ dosage for COD removal. The COD removals during 60 min photolysis time were 33.6%, 52.6% and 64.2% for 5 mM, 10 mM and 15 mM, respectively. At 20 mM H₂O₂ dosage, COD removal was reduced to 54.7% within 60 min of reaction time. This is

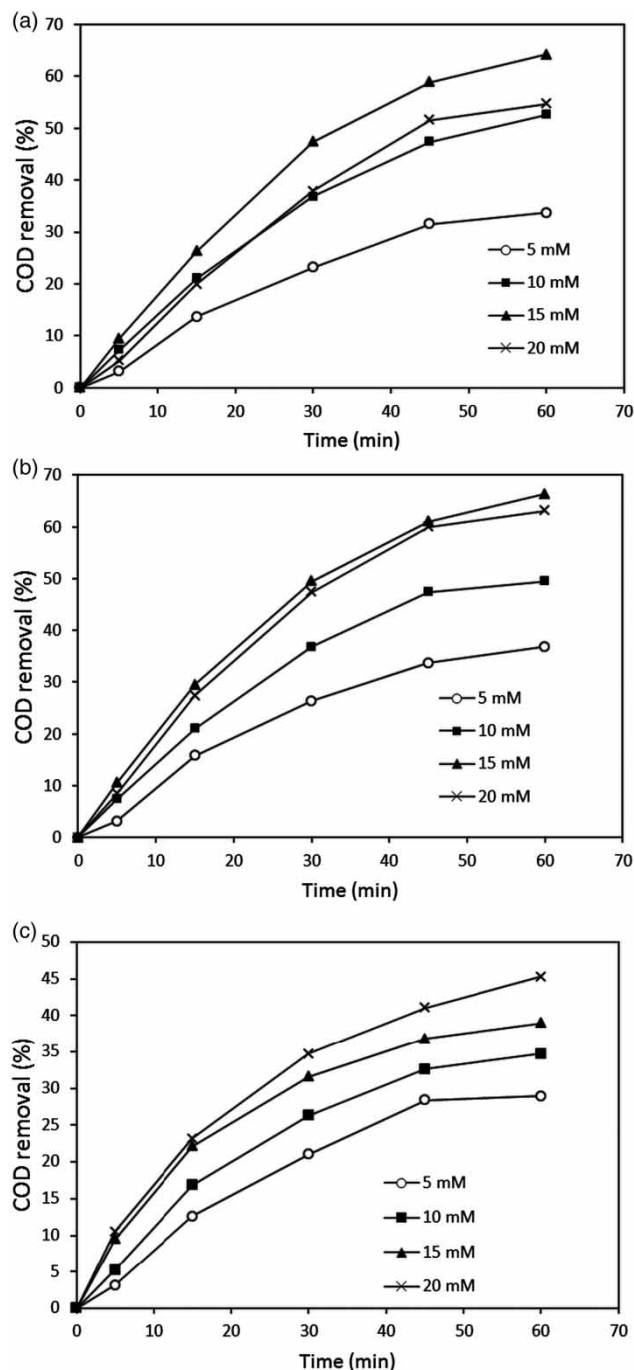


Figure 3 | The effect of oxidant dosage on COD removal in UV/oxidant systems: (a) UV/H₂O₂ (pH 3.0), (b) UV/PS (pH 7.0), (c) UV/PC (pH 3.0).

attributed to increasing H₂O₂ dosage in which excessive H₂O₂ acts as a scavenger for hydroxyl radical. In fact, H₂O₂ has an inhibition effect in higher dosages than the optimum dosage (Yazdanbakhsh *et al.* 2015). The

optimization of oxidant dosage is very important since it not only affects the removal efficiency but it can also increase the cost of the process:

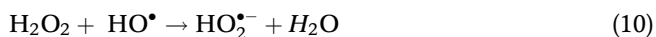


Figure 3(b) shows the influence of oxidant dosage on COD removal from petrochemical wastewater in a UV/PS system at a fixed pH of 7. According to this figure, an increase in PS dosage enhances COD removal efficiencies, as it is possible that the amount of sulfate radicals also rises in solution. COD removals in 60 min reaction time were 36.8%, 49.4% and 66.3% for 5 mM, 10 mM and 15 mM, respectively. When PS dosage was increased to 20 mM, COD removal efficiency slightly decreased to 63.1%. This behavior is related to the reaction of PS with free radicals such as sulfate and hydroxyl radicals. The excessive PS can also be a scavenger for the main oxidizing agents. Indeed, PS competes with free radicals for reaction with organic compounds. Moreover, the peroxydisulfate radical produced has a lower redox potential in comparison with sulfate and hydroxyl radicals (Chu *et al.* 2011; Ahmadi *et al.* 2015). Similar to H_2O_2 , PS had the best performance in 15 mM dosage:



Figure 3(c) displays COD removal efficiencies at various dosages of PC at a constant pH of 3. The results showed that removal efficiencies of COD in UV/PC are highly dependent on PC dosages. An increase in PC dosage increased COD removal. COD removals in 60 min were 28.9%, 34.8%, 39% and 45.2% for 5 mM, 10 mM, 15 mM and 20 mM, respectively. In contrast with PS and H_2O_2 , the scavenging effect was not observed in high PC dosages for degradation of organic compounds. These results showed that more degradation required more oxidant dosage for hydroxyl radical generation.

The effect of ferrous ions

The ferrous ion is the most common catalyst for decomposition of oxidant for free radical generation. In order to assess the effect of Fe^{2+} on COD removal in UV/oxidant

systems, 2 mM of Fe^{2+} was added to the systems. Experimental results are presented in Figure 4. As can be seen, in the presence of the ferrous ion in UV/ H_2O_2 , COD removal efficiency increased from 64.2 to 74.5% after 60 min (Figure 4(a)). The formation of Fenton's reagent (Fe^{2+} and H_2O_2) enhanced the generation of hydroxyl radicals and thus the degradation of organic compounds was boosted. Moreover, regeneration of ferrous ions in UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ improved via UV irradiation and photo-reduction of $\text{Fe}(\text{OH})^{2+}$ as predominant species of Fe^{3+} had a positive effect on the production of HO^\bullet (Zapata *et al.* 2009; Moradi *et al.* 2016):



The ferrous ion also enhanced the UV/PS system, as COD removal efficiency reached 74.5% after 60 min reaction time in comparison with 66.3% (Figure 4(b)). The ferrous ion can decompose PS to the sulfate radical, and accelerates degradation of the organic pollutants using more generation of $\text{SO}_4^{\bullet-}$. It is possible that the reactions of equations 13 and 14 occurred at a solution similar to the UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system. The simultaneous presence of UV and Fe^{2+} could effectively activate PS for petrochemical wastewater treatment.

In the case of UV/PC, the ferrous ion could heighten the removal efficiency significantly; similar to H_2O_2 , Fenton's reagent was formed in solution, raising the oxidation ability of the process for the destruction of organic content. In the presence of Fe^{2+} , COD removal efficiency was 1.26-fold more than in the absence of the ferrous ion (Figure 4(c)).

In the three systems, the COD removal rate was rapid in the first 30 min, which can be attributed to the presence of oxidant at the beginning of the reaction time. After that, the degradation rate decreased due to consumption of the free radicals and oxidant by organic compounds.

The kinetics of COD removal were calculated by the first-order model based on Equation (15):

$$\ln \frac{\text{COD}_t}{\text{COD}_0} = -kt \quad (15)$$

where COD_0 is the initial COD of petrochemical wastewater (mg/L), COD_t is COD at t time (mg/L), k is the constant rate

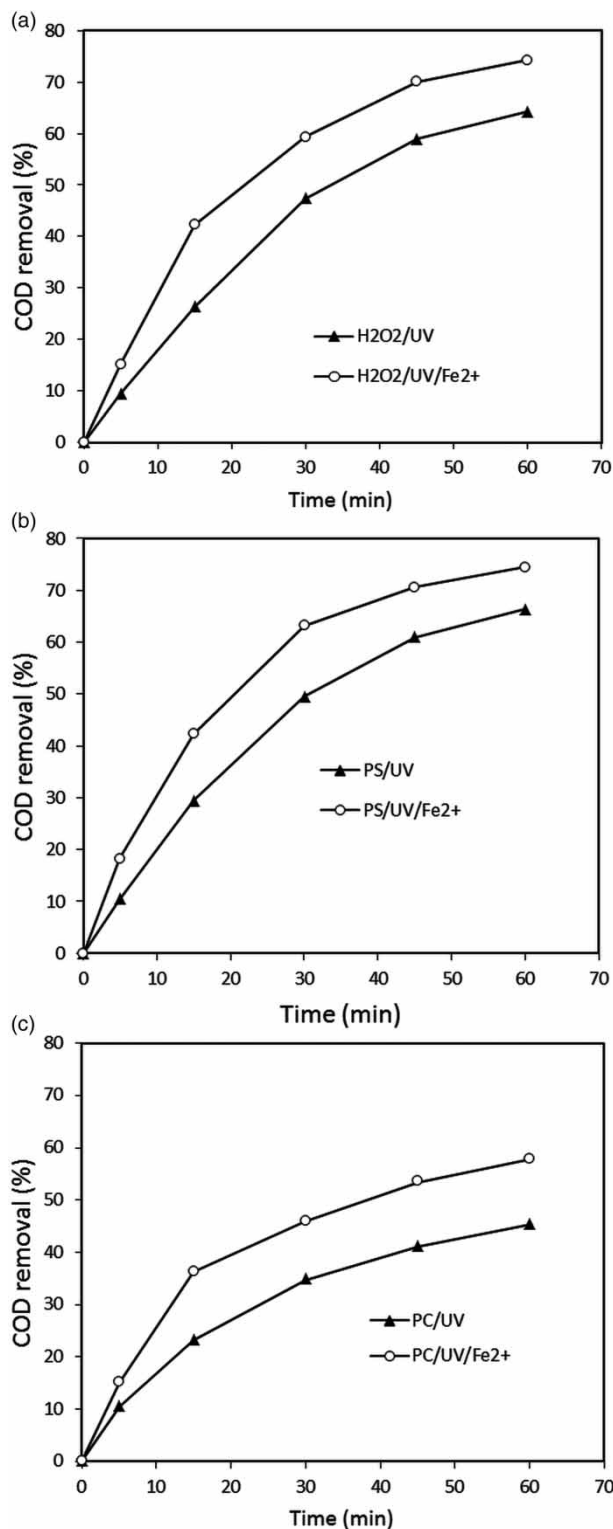
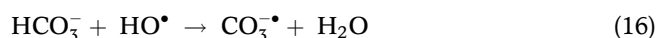


Figure 4 | The effect of ferrous ion (2 mM) on COD removal in UV/oxidants system: (a) UV/H₂O₂ (H₂O₂ = 15 mM, pH 3.0), (b) UV/PS (PS = 15 mM, pH 7.0), (c) UV/PC (PC = 20 mM, pH 3.0).

(min⁻¹). The rate constant of the first-order reaction (k) was gained from the plot of $\ln(\text{COD}_t/\text{COD}_0)$ versus t (irradiation time). The rate constants of the first-order reaction are presented in Figure 5. As can be seen, although the presence of ferrous ions could improve COD removal efficiency in UV/H₂O₂ and UV/PS systems, it had no significant influence on the rate constants of these systems. In this way, the rate constants were 0.018 min⁻¹, 0.0188 min⁻¹, 0.0232 min⁻¹, and 0.0232 min⁻¹ for UV/PS, UV/PS/Fe²⁺, UV/H₂O₂ and UV/H₂O₂/Fe²⁺, respectively. In contrast, a considerable increase was observed in the rate constant of the UV/PC/Fe²⁺ system in comparison with UV/PC. According to the related results, the rate constants of the UV/PC and UV/PC/Fe²⁺ systems were 0.0099 min⁻¹ and 0.0139 min⁻¹, respectively. Not only can the ferrous ion improve the removal efficiency in UV/PC but it also accelerates the degradation rate of organic compounds. However, the photo-oxidation process based on PC had the lowest removal efficiency in comparison to other processes that can be associated with the presence of carbonate anion in PC as a scavenger for hydroxyl radical based on Equations (16) and (17):



Decolorization of petrochemical wastewater by UV/oxidants

The studied petrochemical wastewater had an apparent yellowish color with an absorbance of 0.411 cm⁻¹ at a

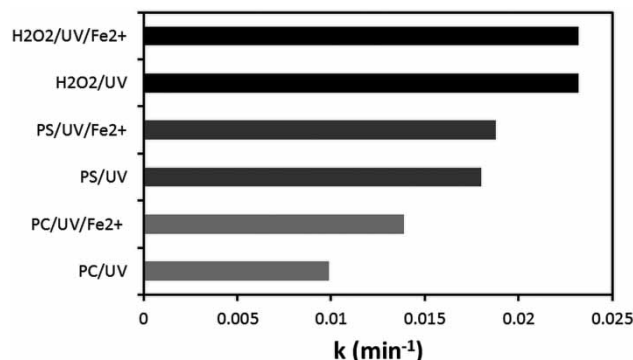


Figure 5 | The rate constants of COD removal in the studied processes.

wavelength of 400 nm. Although the intensity of color of the wastewater is relatively low, the presence of color in industrial wastewater is aesthetically important. The results of photo-oxidation of all the studied processes indicated that the wastewater became colorless after 30 min reaction time (Figure 6). It should be noted that the decolorization was faster in UV/PS and UV/PS/Fe²⁺ systems compared to other ones. These results show that UV/oxidants are effective processes to remove color from petrochemical wastewater.

Biodegradability improvement

Due to the presence of phenolic and toxic compounds, biological processes cannot efficiently treat petrochemical wastewater. On the other hand, AOPs are very expensive when they are used only for the treatment of organic compounds. Due to their capability of improving effluent quality, AOPs are well suited to be used before biological processes. In order to evaluate the biodegradability of treated effluent, the BOD/COD index was selected as the most common index (Moradi & Ghanbari 2014; Yazdanbakhsh *et al.* 2015). The BOD/COD ratio of raw petrochemical wastewater was 0.20, indicating that the biodegradability of this wastewater was low since BOD/COD values of <0.30 signify that biodegradation occurs with difficulty. Figure 7 displays the BOD/COD values after photo-oxidative processes during 60 min of photolysis time. In the cases of UV/PC and UV/PC/Fe²⁺ systems, biodegradability did not

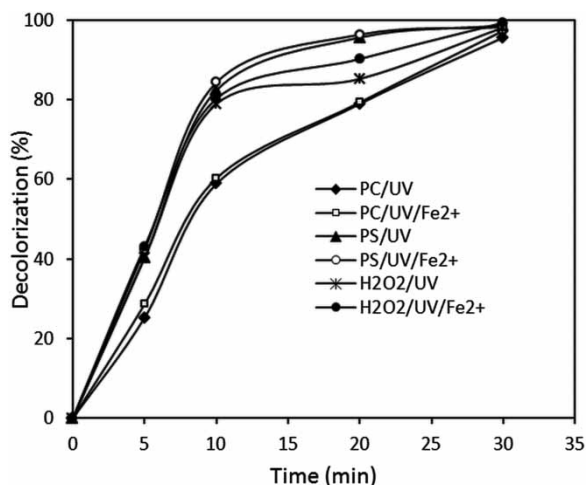


Figure 6 | Decolorization of petrochemical wastewater in UV/oxidant systems (conditions are similar to Figure 3).

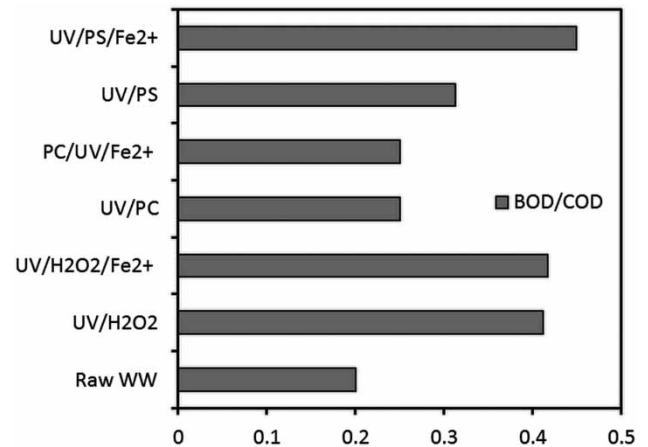


Figure 7 | The BOD/COD values after photo-oxidative processes.

meaningfully increase. The BOD/COD ratio of both systems reached 0.25, which can be attributed to the reduction of the COD value as well as the BOD value in solution. Biodegradability slightly increased, thus the wastewater remained weakly biodegradable. BOD/COD values were markedly increased to 0.41 by UV/H₂O₂ and UV/H₂O₂/Fe²⁺ systems. It has been reported that when the BOD/COD value is >0.4, the wastewater can be considered for biodegradation (Ledezma Estrada *et al.* 2012; Ghanbari & Moradi 2015). It seems that during the treatment of petrochemical wastewater, non-biodegradable matters are converted to biodegradable compounds, since the BOD/COD ratio is increased. This behavior was also observed in the UV/PS/Fe²⁺ process as BOD/COD increased to 0.45, indicating as non-biodegradable compounds are oxidized to simple matters that their biodegradabilities were easier than those of the mother compounds. The BOD/COD value after treatment by UV/PS reached 0.31. A BOD/COD value between 0.3 and 0.4 represents partial biodegradability of wastewater (Soloman *et al.* 2009; Ledezma Estrada *et al.* 2012). The biodegradability improvement of the studied processes followed the order: UV/PS/Fe²⁺ > UV/H₂O₂ ≥ UV/H₂O₂/Fe²⁺ > UV/PS > UV/PC ≥ UV/PC/Fe²⁺.

Cost analysis

Not only does the removal efficiency play an important role in the performance of wastewater treatment processes, but the economic aspect of the process is also a crucial factor

for selection of a suitable system. Cost evaluation of the processes helps decision making in the selection of a suitable process for wastewater treatment.

EEC, the electricity cost and the cost of chemicals were calculated and their results are presented in Table 2. As can be seen, the order of ECC and electrical cost values of the processes followed the COD removal efficiency order based on Equation (8), the fraction numerator is constant for all the processes, while the fraction denominator depends on COD removal efficiency. Hence, with the increase in COD removal efficiency, ECC is decreased. On the other hand, the main costs of chemicals were directly based on the price of oxidants. PC had the lowest price in comparison with other oxidants, thus the chemical costs of the UV/PC and UV/PC/Fe²⁺ processes were less than those of the other ones. In comparison to PS, H₂O₂ was an oxidant with a lower cost. H₂O₂-based processes consume less mass of oxidant in comparison with others due to the low molar mass of hydrogen peroxide. As can be seen, chemical costs have a greater contribution to the total costs of the processes, while electrical costs play a non-significant role in comparison with the chemical costs. Therefore the total cost is highly dependent on chemical cost. Among the oxidants, PC was an inexpensive oxidant compared to the two other oxidants. Accordingly, the order of total costs was: UV/PS/Fe²⁺ > UV/PS > UV/H₂O₂/Fe²⁺ > UV/H₂O₂ > UV/PC/Fe²⁺ > UV/PC.

In order to select a suitable process for petrochemical wastewater, various parameters should be considered such as efficiency, cost benefit, the target of the process, the impacts of the process on the environment and effluent

(Ghanbari & Moradi 2015). As a conclusion, UV/H₂O₂/Fe²⁺ and UV/H₂O₂ were effective and economic processes for COD removal from petrochemical wastewater. Moreover, H₂O₂ is a green chemical, since its residuals are oxygen and water which does not increase the dissolved solids of the effluent, while PS and PC affect the salinity of the effluent by function groups of sulfate and carbonate along with sodium metal (Anipsitakis & Dionysiou 2003; Neyens & Baeyens 2003).

CONCLUSIONS

In this study, the performances of UV/H₂O₂, UV/PS and UV/PC systems for COD removal from petrochemical wastewater were evaluated. UV/PC and UV/H₂O₂ systems had better efficiency at pH 3.0, while pH 7.0 was appropriate for the UV/PS system. The presence of the ferrous ion increased the COD removal efficiency of UV/oxidants, especially in the case of the UV/PC system. However, UV/PC and UV/PC/Fe²⁺ could not effectively remove COD from petrochemical wastewater whereas UV/H₂O₂ and UV/PS eliminated nearly 70% of COD. Complete decolorization occurred at only 30 min reaction time for all studied processes. The biodegradability enhancement of the studied processes followed the order: UV/PS/Fe²⁺ > UV/H₂O₂ ≥ UV/H₂O₂/Fe²⁺ > UV/PS > UV/PC ≥ UV/PC/Fe²⁺. Moreover, cost analysis showed that the chemicals' cost is more than the electrical cost in photo oxidation processes. Finally, we concluded that H₂O₂-based processes are environmentally friendly and effective for petrochemical wastewater treatment.

Table 2 | ECC, electrical cost, chemical cost and total cost of the studied processes at 60 min reaction time

Processes	Parameters			
	ECC (kWh/kg _{COD removed})	Electrical cost (US\$/ kg _{COD removed})	Chemical cost (US\$/ kg _{COD removed})	Total cost (US\$/ kg _{COD removed})
UV/PC	186.04	2.73	9.11	11.84
UV/PC/Fe ²⁺	145.69	2.14	10.87	13.01
UV/H ₂ O ₂	131.14	1.92	11.25	13.17
UV/H ₂ O ₂ /Fe ²⁺	113.33	1.66	13.01	14.76
UV/PS	127.01	1.86	21.1	22.96
UV/PS/Fe ²⁺	113.03	1.66	22.86	24.52

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