

## COMPARATIVE STUDY FOR ACTIVATION OF HYDROGEN PEROXIDE BY CHEMICAL REAGENTS ( $Fe^{2+}$ , $Al^{3+}$ ) TO REDUCE CHEMICAL OXYGEN DEMAND IN PETROCHEMICAL WASTEWATER

M.S. Bala<sup>1\*</sup>, A.A. Mohd Azoddein<sup>1</sup>,  
M.I. Ahdash<sup>1</sup>, and B.Y. Alshwal<sup>1</sup>.

<sup>1</sup> Chemical & Natural Resources Engineering, University Malaysia Pahang,  
Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia

### ABSTRACT

*Environmental pollution by toxic compounds is gaining wider concern in modern developed society. The petroleum refining industry produces a large amount of wastewater due to the amount of water used in refining the processes, particularly for cooling systems and lead to increasing wastewater that will impact the environment. The aim of this research is to reduce chemical oxygen demand (COD) in petrochemical wastewater by activation of hydrogen peroxide using two different reagents ( $Fe^{2+}$ ,  $Al^{3+}$ ). In this research was compared several parameters to COD removals such as the effects of concentration / dosage of  $H_2O_2$ , concentration, and dosages of  $Al_2(SO_4)_3$  and concentration and dosages of  $FeSO_4$  on the removal efficiency of COD. In this study is proven the effect of Fenton's reagent process besides the dosage between hydrogen peroxide ( $H_2O_2$ ) and ferrous ion ( $Fe^{2+}$ ) in the reagent that Fenton process was highly efficient to decrease COD and total suspended solid (TSS) reduction. However, addition of aluminium with hydrogen peroxide does not have any effect to remove COD. The result found that overall removal was achieved by 70% in term of COD, and 88 % in term of TSS using Fenton's reagent process.*

**KEYWORDS:** Petrochemical wastewater; COD; hydrogen peroxide; Fenton's reagent process; reagents ( $Fe^{2+}$ ,  $Al^{3+}$ ) process.

### 1.0 INTRODUCTION

Nowadays environmental pollution by toxic compounds is gaining wider concern in modern developed society. Therefore, regulations regarding the release of effluents are of increasing severity and research efforts are underway to develop powerful oxidation techniques for avoiding dangerous accumulation of toxic organics in the aquatic environment. The treatment of wastewater generated by industrial activity is a major concern for plant operators and in particular those of refineries and petrochemical units. The petroleum refining industry produces a large amount of wastewater due to the amount of water used in refining the processes, particularly for cooling systems (Mizzouri & Shaaban 2013; Al-Malack 2013). Generally, petroleum refineries generate polluted wastewater containing approximately 150-250 mg/L of chemical oxygen demand (COD), phenol and oil levels of 20-200 mg/L and 100-300 mg/L, by against desalted water in tank's bottoms and up to 5000 mg/L (Al-Malack 2013).

---

\* Corresponding Email: kingpop\_star@yahoo.com

Moreover, some techniques should be developed in order to effectively remove organic and inorganic pollutants to improve the general quality of discharged wastewater. Advanced oxidation processes (AOPs) based on the generation of hydroxyl radicals (OH) are widely used in the treatment or pretreatment of bio-refractory industrial wastewater. Among the AOPs, Fenton process is particularly attractive because of its simplicity and high removal efficiency of recalcitrant pollutant (Jagadevan et al. 2011; Karthikeyan et al. 2011).

According to the existing form of catalyst, the Fenton reaction can be divided into two types, namely the classical homogeneous Fenton oxidation and the novel heterogeneous Fenton oxidation. Additionally, most heterogeneous Fenton technologies are still in the stage of laboratory research, which are difficult for the industrial application (Hassan & Hameed 2011). In addition, Fenton oxidation has been extensively studied for treatment of a variety of toxic and bio-refractory wastewaters such as chemical manufacturing wastewater (Diya'uddeen et al. 2011; Padoley et al. 2011).

There are many applications as to remove COD. However, this research will focus on using hydrogen peroxide to reduce COD by direct oxidation (either complete or partial) of wastewater components. The rate and extent of oxidation depend on the H<sub>2</sub>O<sub>2</sub> concentration and the nature of the waste being treated. The use of iron-catalyzed H<sub>2</sub>O<sub>2</sub> (Fenton's reagent) can further increase the amount of COD reduction achieved (Chu et al. 2012). Moreover, using of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> to reduce the amount COD is tested and compared, which one will be more suitable treatment for petrochemical wastewater. On the other hand, hydrogen peroxide was found to be environmentally safe, cost effective and easy to operate.

## 2.0 METHODOLOGY

### 2.1 Petrochemical Waste Water Sample

The sample of petrochemical wastewater was purchased from the East Coast petrochemical industry, which is approximately 110 km to the south of Kuala Terengganu and the production of this industry involved in the sample petroleum gas production. While COD was very low in petrochemical wastewater was added the components of ammonium chloride (NH<sub>4</sub>Cl), potassium dihydrogen phosphate anhydrous (KH<sub>2</sub>PO<sub>4</sub>) and calcium carbonate powder (CaCO<sub>3</sub>) to increase COD based on Siddique et al., (2011). See Table 1. Then, the sample used for the oxidation experiments was firstly characterized in terms of alkalinity measure (pH), total suspended solids (TSS) and COD.

Table 1. Synthetic influent composition

Chemical compounds	g
Calcium carbonate powder cp bendosen (CaCO <sub>3</sub> )	1.8
Ammonium Chloride (NH <sub>4</sub> Cl)	1.8
Potassium Dihydrogen Phosphate anhydrous (KH <sub>2</sub> PO <sub>4</sub> )	0.250

## 2.2 Materials

The main material used in this study is hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (30 % w/w), which was obtained from HMBG company. Other materials such as the iron (II) sulphate heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O) and aluminium sulphate hydrate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.16H<sub>2</sub>O, 98 %) were obtained from SIGMA-ALDRICH. Moreover, Fenton process reagent consists of iron (II) sulphate heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution are shown in Table 2, complete with other chemicals used in during the experiments.

Table 2. Chemicals was used for the experiment

Items	Packing	Brand	Code
Hydrogen peroxide 30% w/w ( 100vol ) prs, panreac* * xi 5.1/ii (H <sub>2</sub> O <sub>2</sub> )	Liter	HMBG	C0370
Aluminium sulfate hydrates 98%	500g	SIGMA-ALDRICH	368458
Iron(II) sulphate heptahydrate ( FeSO <sub>4</sub> . 7H <sub>2</sub> O)	1000g	SIGMA-ALDRICH	231-753-5
Calcium carbonate powder cp bendosen	500g	BENDOSEN	C1560
Ammonium Klorida (Ammonium Chloride), 99.8% ChemAR	1000g	SYSTEM	235-186-4
Potassium Dihydrogen Phosphate anhydrous C.P.	1000g	R&M	1802
COD Digestion Vials, High Range, pk/25	20-1500	HACH	2125925

## 2.3 Equipments

### 2.3.1 pH meter

The Mettler Toledo pH meter was used to measure the pH value of the wastewater sample.

### 2.3.2 Chemical Oxygen Demand

Chemical Oxygen Demand (COD) was analyzed using the HACH Method. 14 HACH test tubes. A mixture of concentrated sulphuric acid and standard potassium dichromate has been prepared. The first test tube was used as blank and other twelve were used as sample run. The sample is then diluted with the dilution factor of 9. Then, 2 mL of deionized water is added into an empty first test tube as the blank test tube and 2 mL of diluted sample is added into the 14 HACH test tubes was added into each sixteen test tube. The mixtures of 14 test tubes were refluxed for 2 hours in the HACH COD Digestion Reactor. Then the samples were then analysed by using DR2800 Spectrophotometer to determine the COD content in each sample. The removal efficiency (Removal (%)) was calculated from the following formula (Sayuti & Azoddein 2015), as given by Equation (1).

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where  $C_o$  is the initial COD of sample and  $C_t$  is the COD of sample at time t.

### 2.3.3 Portable Spectrophotometer

A portable spectrophotometer (model HACH DR2800) was used to analyze the COD HR value of the vial reagent.

### 2.3.4 Total suspended solids

The suspended solid was analyzed by using gravimetric method (APHA, 1985). Major equipment consists of TSS test of two types of rocker vacuum pump (300) and All-glass filtration assembly was used to analyze suspended solids value contain in the wastewater

The TSS in the wastewater samples were calculated using the following formula Equation (2) and Equation (3).

$$\text{TSS} = \frac{W_B - W_A}{\text{Sample volume}} \times 100 \tag{2}$$

where  $W_A$  = Initial Weight of filter paper  
 $W_B$  = Final Weight of filter paper.

$$\% \text{ Removal} = \frac{TSS_o - TSS_t}{TSS_o} \times 100 \tag{3}$$

where  $TSS_o$  = Initial turbidity of sample  
 $TSS_t$  = Turbidity of the sample at time t

## 3.0 RESULTS AND DISCUSSION

### 3.1 The Petrochemical Wastewater Characteristics

The petrochemical wastewater sample was taken from the east coast petrochemical industry. The characteristic of the industrial petrochemical wastewater are shown in Table 3.

Table 3. The characteristic of the industrial petrochemical wastewater

Parameter	Units	Petrochemical wastewater effluent	Standard	
			A	B
pH	pH	8.73	6.0–9.0	5.5 – 9.0
Chemical Oxygen Demand	mg/L	576	< 50	< 100
Suspended Solid	mg/L	0.011	< 50	< 100

### 3.2 Experimental results

The experimental results of the research were shown in Tables 4 (using Fenton reagent), which indicated that the range of percentages of removal of in the effect of dosages was 68 % and 70 % for COD and 82 %, 88 % for TSS and 7.30 and 2.51, respectively.

Table 4. The percentage removal of COD and Suspended Solids for Fenton reagent on the effect of dosages

Number	(g) Fe <sup>2+</sup>	(mL) H <sub>2</sub> O <sub>2</sub>	pH	% Removal	
				COD	TSS
1	0.5	1.4	7.44	50	73
2	0.5	1.6	7.39	66	79
3	0.5	1.8	7.30	68	82
4	0.5	1.65	6.46	28	80
5	0.7	1.65	6.82	32	81
6	1.1	1.65	2.74	59	79
7	1.3	1.65	2.51	70	88

On the other hand, Al<sup>3+</sup> with different dosage has no effect on COD removal as shown in Table 5. However, the percentage of TSS removal was 55 % - 82 % and pH was 7.06 - 3.77.

These were achieved at by adopting Fe<sup>2+</sup> dosage of 1.3 g and H<sub>2</sub>O<sub>2</sub> dosage of 1.65 mL, the maximum removal percentages of COD and TSS are observed, 70% and 88%, respectively.

Table 5. The percentage removal of COD and Suspended Solids for aluminium ion reagent on the effect of dosages

Number	Al <sup>3+</sup> (g)	H <sub>2</sub> O <sub>2</sub> (mL)	pH	% Removal	
				COD	TSS
1	0.5	1.4	7.12	-	55
2	0.5	1.6	7.08	-	55
3	0.5	1.8	7.06	-	18
1	0.5	1.65	4.46	-	82
2	0.7	1.65	4.46	-	64
3	1.1	1.65	3.87	-	45
4	1.3	1.65	3.77	-	65

#### 3.2.1 Effect of dosages of Hydrogen Peroxide in Fenton process

The first parameter into considering in this Fenton oxidation is the dosages of H<sub>2</sub>O<sub>2</sub> required for maximum efficiency to obtain the best efficiency in the treatment. In this sense, experiments were performed by fixing the Fe<sup>2+</sup> dosage and change the value of H<sub>2</sub>O<sub>2</sub> dosages was varied as shown in Figures 1(a), (b) and (c). Significant enhancement of efficiency was observed when the H<sub>2</sub>O<sub>2</sub> dosage was increased from 1.4 mL to 1.8 mL, where the removal percentages of COD and TSS increase to 68 % and 82%, respectively.

Beside that the effect of pH was a decrease with different dosages of  $H_2O_2$ . As reported by (Lou & Huang, 2009) increasing the dosage of hydrogen peroxide would result in more production of hydroxyl radicals (have high oxidation potential), which could enhance the oxidation capacity of the system.

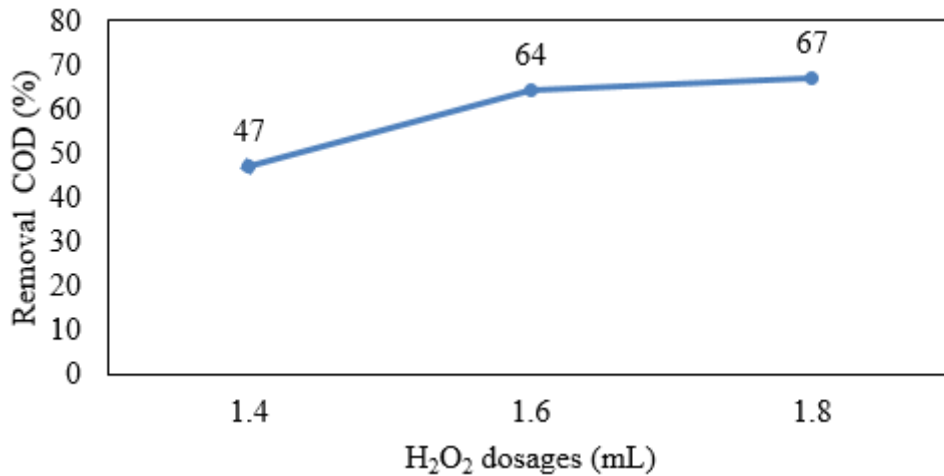


Figure 1(a). Effect of the dosages of  $H_2O_2$  for COD removal

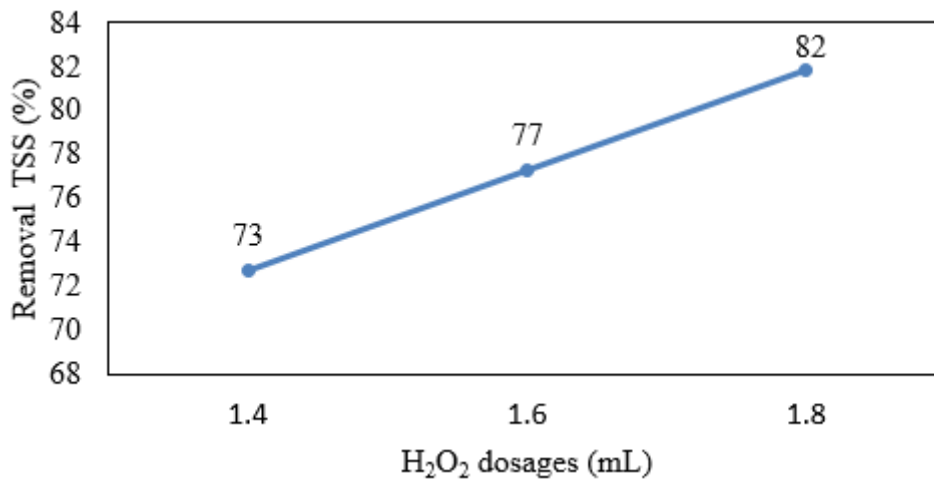


Figure 1(b). Effect of  $H_2O_2$  dosages for TSS removal

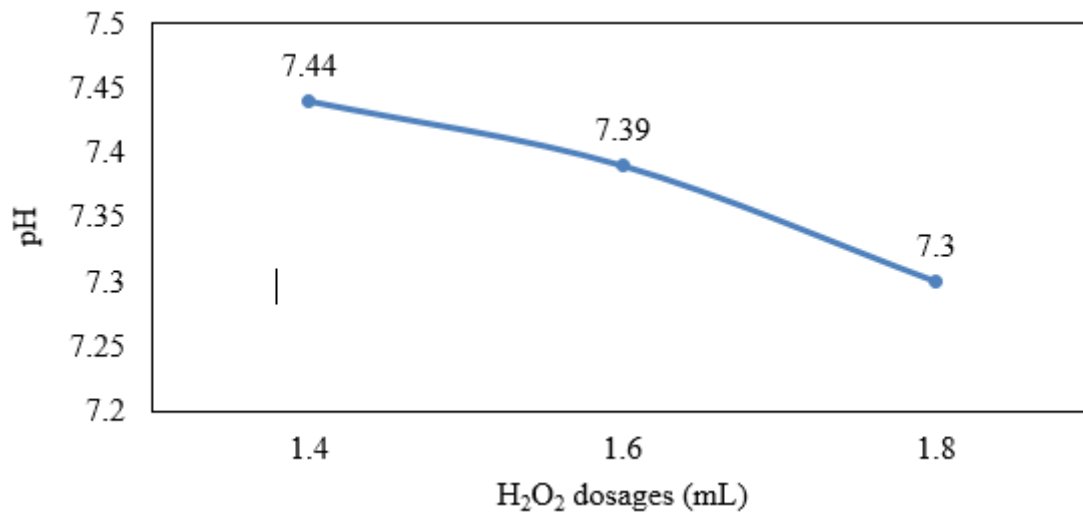


Figure 1(c). Effect of  $H_2O_2$  dosages for pH.

However, the excess dosage of H<sub>2</sub>O<sub>2</sub> does not warrant a progressive increase of removal efficiency, due to the fact that at the end of the graph shown the percentage of removal does not increase too much compared than when dosages from 1.4 mL until 1.6 mL. This happened because of some of the hydroxyl radicals would be scavenged by excess H<sub>2</sub>O<sub>2</sub>, through the Equation (4) which is



In the case of excess H<sub>2</sub>O<sub>2</sub> existed in the system (Lunar et. al. 2000), it is given by Equation (5).



As a consequence, the variation of removal percentage was slight when excess H<sub>2</sub>O<sub>2</sub> was added into the system. However, it is important to note that the amount of but the fact is the importance of H<sub>2</sub>O<sub>2</sub> is very much closely related to the dosages of •OH generated. Typically, the removal efficiency increases with respect to the High activity of OH removal will high.

### 3.2.2 Effect of dosages of Ferrous Ion in Fenton process

Another important detrimental parameter considered in the current study is the required dosages of Fe<sup>2+</sup>, so as to obtain the best percentage removal efficiency in the treatment. Conversely, this experiment was performed by fixing the H<sub>2</sub>O<sub>2</sub> dosages and change the Fe<sup>2+</sup> dosages. The results are shown in Figures 2(a), (b) and (c). Note that all the parameters are mutually proportional as Fe<sup>2+</sup> dosages increases, the removal percentages of COD and TSS removal also increase as well. However, the effect of pH was to decrease with different dosages of Fe<sup>2+</sup>. The percentage of removal is relatively high compared to that of the dosages of Al<sup>3+</sup>.

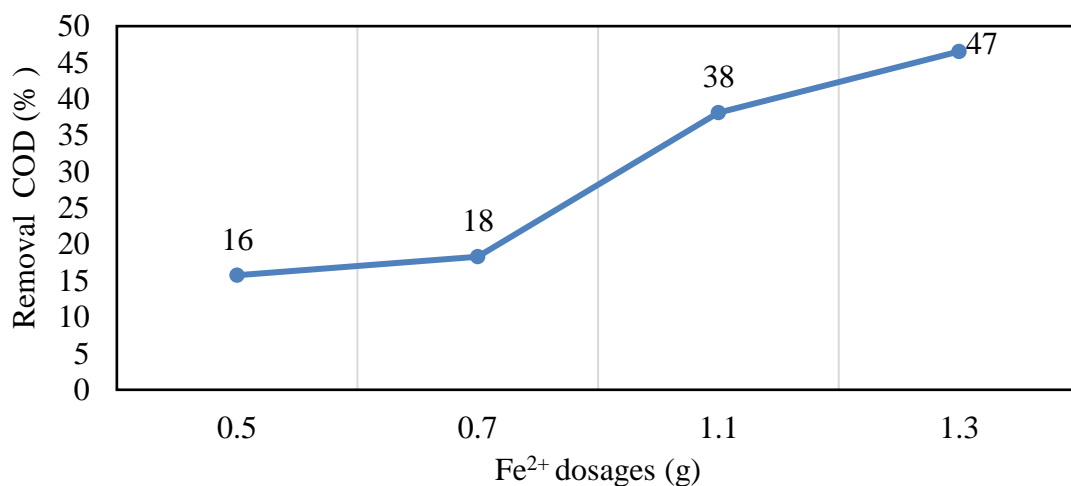


Figure 2(a). Effect of the dosages of Fe<sup>2+</sup> for COD removal

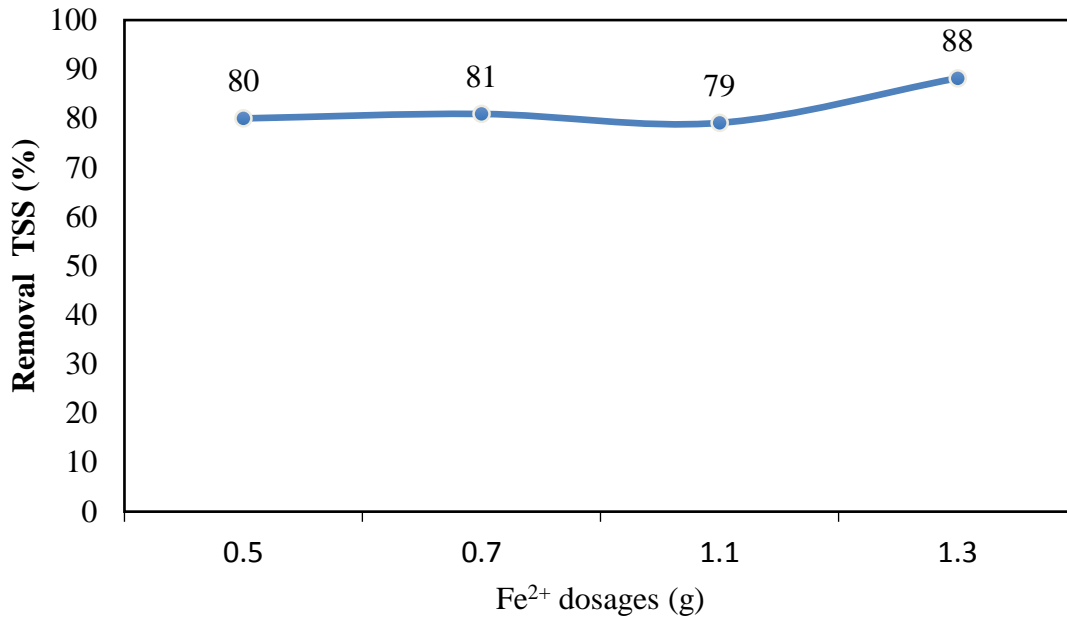


Figure 3.2.b: Effect of the dosages of Fe<sup>2+</sup> for TSS removal.

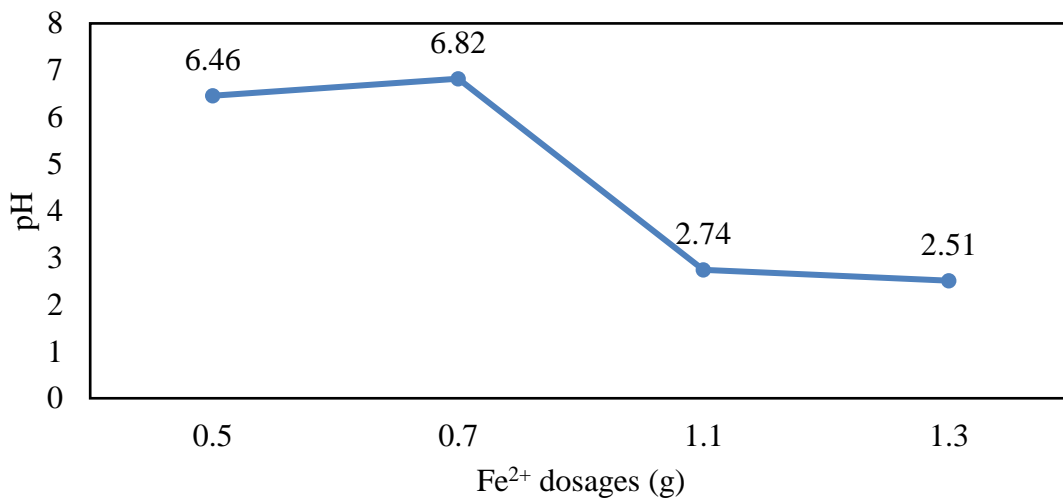


Figure 2(c). Effect of the dosages of Fe<sup>2+</sup> for pH

For this experiment, percentage removal of all the parameters is higher than the previous. The percentage of removal of COD and TSS were achieved until 70% and 88%, respectively. According to Xing et al., (2010), the oxidation rate for TSS increases with respect to the Fe<sup>2+</sup> concentration due to the as the result of higher production of hydroxyl radicals as given by Equation (6).



The hydrogen peroxide is not a very strong oxidant. The extra chemical must be reacted with the oxidising power of hydrogen peroxide, sine it was not enough to destroy large molecules. Hence, other chemical needed to react with hydrogen peroxide to produce hydroxyl free radical ion which is a very strong oxidation agent. According to



Xing et al., (2010), the number of ferrous ions added are related to the amount of hydroxyl free radicals produced.

The pH decreased and the removal efficiencies of COD and TSS do not increase significantly when the dosage of ferrous ions increases from 0.5 g to 1.3 g. This phenomenon might be due to the situation that when the ferrous ions and hydroxyl free radicals are high; the ferrous ions can react with the hydroxyl free radicals according to Equation (7). Here the concentrations of ferrous ions and hydroxyl free radicals are high.



Hence, the excess ferrous ions consume the hydroxyl free radicals with a high oxidative potential. In spite of the improvement in reaction kinetics achieved by adopting higher  $\text{Fe}^{2+}$  concentration, the production of  $\text{Fe}^{3+}$  that will probably precipitate as  $\text{Fe}(\text{OH})_3$ .

### 3.2.3 Effect of Doses Of Aluminum Ion And Dosages of $\text{H}_2\text{O}_2$

In this study,  $\text{Al}^{3+}$  with different dosages has no effect on COD removal. The results showed that by  $\text{Al}^{3+}$  fixing at 0.5 g with change dosages of  $\text{H}_2\text{O}_2$  (1.4, 1.6 and 1.8 mL), the TSS removal were 55 %, 55 % and 18 % respectively. Figure 3(a) shows the removal percentage of TSS decreased from 55 % to 18 % and Figure 3(b) indicates the effect of pH was decreased from 7.12 to 7.06.

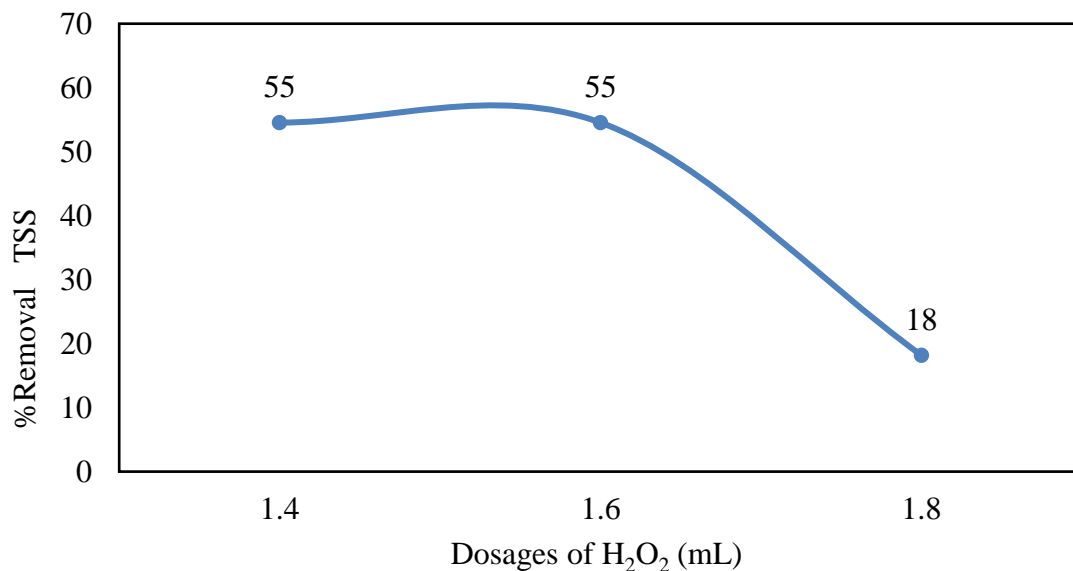


Figure 3(a). Effect of the dosages of  $\text{H}_2\text{O}_2$  for TSS removal

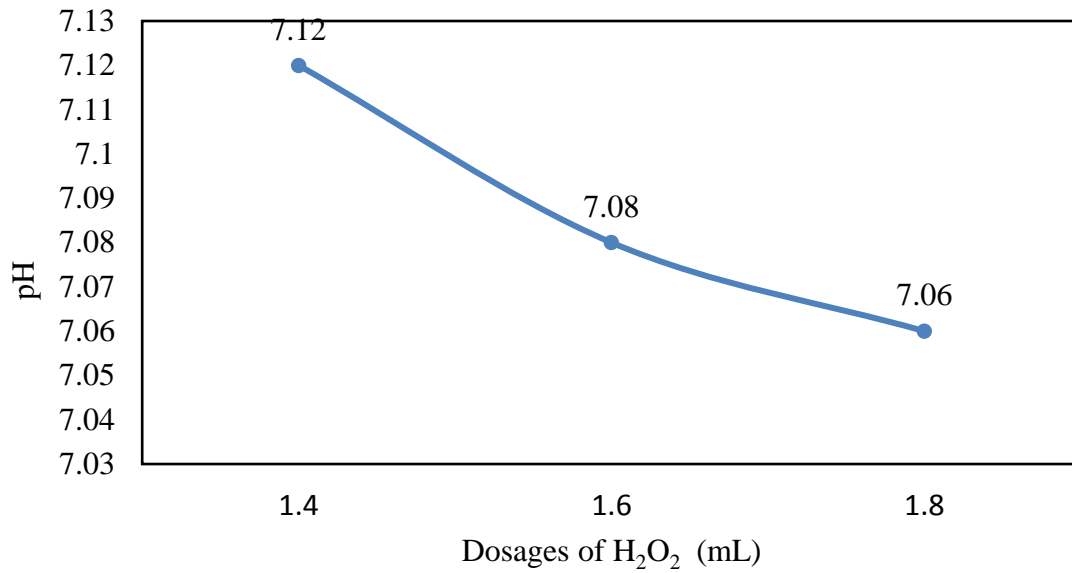


Figure 3(b). Effect of the dosages of H<sub>2</sub>O<sub>2</sub> for pH

Figure 4(a) shows the percentages of TSS removal when HO<sub>2</sub>O<sub>2</sub> is limited to 1.65 mL with the change dosages of Al<sup>3+</sup> (0.5, 0.7, 1.1 and 1.3 g) were 82 %, 64 %, 45 % and 65 % respectively. It was shown that a drop from 82 % to 45 % at 1.1 g of Al<sup>3+</sup>, and then suddenly increased to 65 % at 1.3 g of Al<sup>3+</sup>.

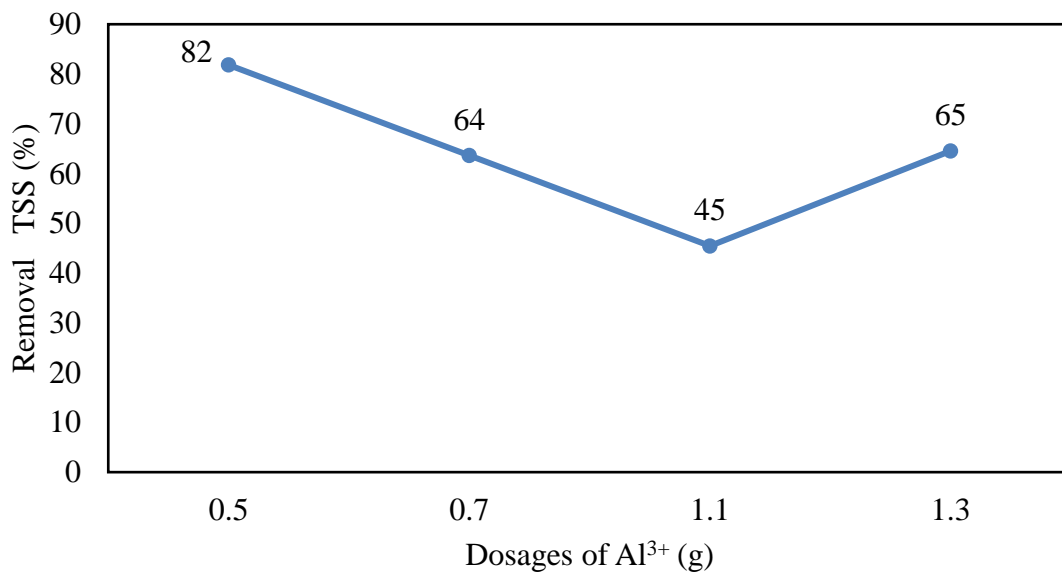


Figure 4(a). Effect of the amount of Fe<sup>2+</sup> for TSS removal

Figure 4(b) shows the effect of pH when the dosages of  $\text{Al}^{3+}$  varied from 0.5 mL to 1.3 mL. The pH started to change when more than 0.7 dosages of  $\text{Al}^{3+}$  was added. Here the pH decreased from 4.46 to 3.77.

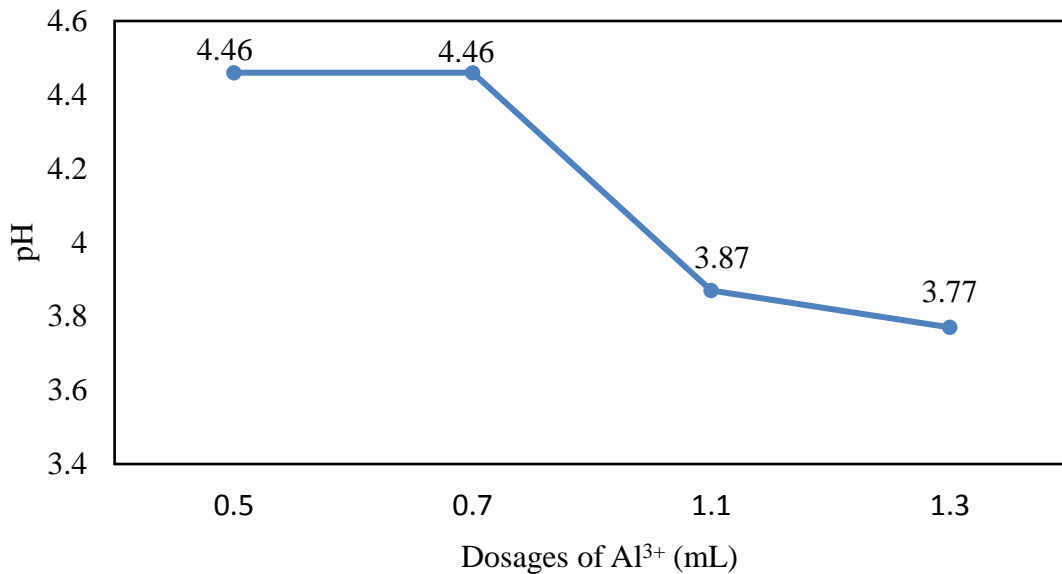


Figure 4(b). Effect of the dosages of  $\text{Fe}^{2+}$  for pH

#### 4.0 CONCLUSION

Petrochemical wastewater can be treated effectively by various chemical treatment processes. This study showed that the Fenton process is an efficient method of treating petrochemical wastewater. Chemical oxygen demand and total suspended solid were reduced by more than 90 % removal and this is a positive result for using activation of hydrogen peroxide with ferrous in petrochemical wastewater. The procedure described here can be proposed as an alternative method for treating the wastewater in Malaysia. This would provide the economic advantage and effective solution for the petroleum industries and industries.

The range in removing all the parameters is between 70 % to 88 %. The best dosage of Fenton reagent is when  $\text{H}_2\text{O}_2$  at 1.65 mL and  $\text{Fe}^{2+}$  amounted to 1.3 g.

The feasibility or effectiveness of this treatment was controlled by the activity of hydroxyl free radicals ions (very strong oxidation agent) produced. Increasing the number of free radicals ions produced will increased the ability of Fenton reagent treatment to destroy large molecules of pollutants in the wastewater.

#### ACKNOWLEDGEMENT

The authors would like to express their gratitude to the Universiti Malaysia Pahang for support of this research and use of laboratory facilities.

## REFERENCES

- Al-Malack, M. (2013). Treatment of petroleum refinery wastewater using crossflow and immersed membrane processes. *Desalination and Water Treatment*, 51(37-39):6985-6993.
- Chu, L. et al., (2012). Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. *Chemosphere*, 86(4):409-414.
- Diya'uddeen, B., Daud, W. & Aziz, A. (2011). Treatment technologies for petroleum refinery effluents: a review. *Process Safety and Environmental protection*, 89(2): 95-105.
- Hassan, H. & Hameed, B., 2011. Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of Reactive Blue 4. *Chemical Engineering Journal*, 171(3): 912-918.
- Jagadevan, S., Dobson, P. & Thompson, I. (2011). Harmonisation of chemical and biological process in development of a hybrid technology for treatment of recalcitrant metalworking fluid. *Bioresource Technology*, 102(19):8783-8789.
- Karthikeyan, S. et al., 2011. Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes. *Desalination*, 281(2011):438-445.
- Lunar, L., Sicilia, D., Rubio, S., Pérez-Bendito, D., & Nickel, U. (2000). Degradation of photographic developers by Fenton's reagent: condition optimization and kinetics for metol oxidation. *Water Research*, 34(6), 1791-1802.
- Mizzouri, N. & Shaaban, M. (2013). Individual and combined effects of organic, toxic, and hydraulic shocks on sequencing batch reactor in treating petroleum refinery wastewater. *Journal of Hazardous Materials*, (250-251):333-344.
- Padoley, K., Mudliar, S. & Banerjee, S. (2011). Fenton oxidation: A pretreatment option for improved biological treatment of pyridine and 3-cyanopyridine plant wastewater. *The Chemical Engineering Journal*, 166(1):1-9
- Siddique, M. et al. (2011) Temperature and Organic Loading Rate Influence on Biomethanation of Petrochemical Wastewater using CSTR. *International Journal of Civil Engineering and Geo-Environment*, 2(1):1-5.