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Oxidation of sulfide removal from petroleum refinery wastewater by using hydrogen peroxide

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Abstract. Petroleum refinery wastewater typically has high concentration of sulfide which is known as the most hazardous pollutants. It is released to the environment either as dissolved sulfide (S^{2-} and HS^-) in effluents or as H_2S in waste gases. The objective in this study is to determine the effectiveness of hydrogen peroxide (H_2O_2) in sulfide removal. The best sulfide concentration, dosage and reaction time were determined. The removal of sulfide from petroleum refinery wastewater via oxidation method by using hydrogen peroxide (H_2O_2) is presented in this study. The treated wastewater was analyzed by spectrophotometer. Result shows that the best concentration of sulfide simulated wastewater (300 mg/L), H_2O_2 dosage (1.5 ml) and reaction time (30 min) able to reduce 97.67%, 98.22% and 98.89% of sulfide concentration from simulated wastewater. Thus, sulfide removal from the actual petroleum refinery wastewater which is spent caustic by using H_2O_2 was able to reduce 99.83% (0.5 mg/L) sulfide concentration. Besides that, Chemical Oxygen Demand (COD) concentration was reduced to 98.29% (70 mg/L) and pH 8.41 after treatment. Thus, it is concluded that oxidation method by using H_2O_2 is effective in sulfide removal as well as COD, and pH from spent caustic. It does meet requirement from Department of Environment (DOE) for sulfide, COD and pH which are 0.5 mg/L, 100 mg/L and 5.5 – 9.0, respectively. The information obtained from this study is useful for scale up purpose in the petroleum refining industry that choose H_2O_2 via oxidation method to remove sulfide from spent caustic wastewater.

1. Introduction

Petroleum refining industries are industrial process plants where natural raw materials such as crude oil and natural gas are processed and refined into more useful products such as petroleum naphtha, gasoline diesel fuel, asphalt base, heating oil, kerosene and liquefied petroleum gas. However, this industry often generates effluents which vary widely in terms of quality and quantity. Specifically, petroleum refinery effluents, generated by the catalytic hydrocracking and refining of various crude-oil fractions contain hydrocarbons. In addition to this, large amounts of nitrogen and sulfur, in the form of ammonia (NH_3) and hydrogen sulfide (H_2S) respectively, are also present [1]. On the other hand, spent caustic or used caustic soda is one of the types of wastewater from the petroleum refining industry. This specifically comes from refinery units such as kerosene treating unit (KTU) tank. It is well known that caustic soda is widely used in the petroleum industry as scrubbing solutions for the removal of acidic components such as naphthenic acid, hydrogen sulphide and cresylic acids from the refined product stream [2]. Hence, once most of the NaOH reacts with sulfur compounds, the solution is known as spent caustics. The resulting wastewater contains high concentration of sulfide which is known to be highly reactive and odorous. Spent sulfidic caustic typically have a pH > 12 and sulphide (S^{2-} and HS^{-}) concentrations exceeding 2-3 wt%. According to the study conducted by [3], it was reported that sulfide concentration of spent caustic from the refinery is 34,517 mg/L. However, spent caustic from the KTU tank typically has high chemical oxygen demand (COD), ranging from 50 000 mg/L to 150 000 mg/L [4].

As stated, sulphides and mercaptans have very strong odours. The odour thresholds for these types of compound are generally in the order of magnitude of parts per billion. Hydrogen sulphide (H_2S) is very insidious because even at low concentration of about 30 mg/L, it can destroy the sense of smell. In fact, at a concentration of about 700 mg/L, death can occur with just a few breaths. Other than that, it is highly toxic, causes unpleasant odour and can easily spoil product. Notably, they lead to corrosion of concrete and metallic structures due to their acidity, which often pose grave challenges to oil storage, use and handling [5]. Furthermore, spent caustic wastewater can cause serious corrosion to the eyes and it also leads diseases associated with the corneal. Specifically, it may cause serious irritation, redness and tearing, blurred vision and conjunctivitis and at last blindness. Likewise, inflammation and blistering can occur if it comes in contact with the skin. As such, releasing spent caustic to water or soil would lead to persistence of its constituents in the soil because it is not likely to volatilize to the atmosphere. In Malaysia, it is well known that the wastewater needs to meet the specification and requirement of Malaysian's Department of Environment (DOE) before being release to the environment. According to [6], the acceptable condition for discharge of Industrial Effluent of standard B, for total sulfide concentration in wastewater is 0.50 mg/L. To comply with the regulation, there are several treatment processes for petrochemical refinery wastewater. Most of these focuses on the reduction of sulfide and other harmful chemicals. Notable among these processes are chemical precipitation [7], electrochemical [8], electrocoagulation [9], and photocatalytic degradation [10]. Unfortunately, spent caustic wastewater does not allow direct biological treatment, even after neutralization and dilution. In fact, direct neutralization of spent caustics has the potential to produce toxic hydrogen sulfide [5].

Therefore, the sulfide concentration in spent caustic wastewater still exceeds the limit of acceptable discharge condition of Industrial Effluent of standard B. Release of petroleum refinery wastewater which consists dissolved sulfide (S^{2-} and HS^{-}) in effluents and H_2S in waste gases brings harm to human and environment as well. This study aims to removes sulfide via oxidation method by using hydrogen peroxide (H_2O_2). Oxidation method is used to remove sulfide (S^{2-}) as sulfate (SO_4^{-2}) without the released or production of hydrogen sulfide (H_2S) from petroleum refinery wastewater. Hydrogen peroxide (H_2O_2), being a strong oxidant will be used for this chemical oxidation to reduce sulfide in wastewater. Although it is typically expensive treatment compared to physical and biological treatment, hydrogen peroxide (H_2O_2) can be used as an improvement of existing physical or biological treatment processes, according to the situation. In the chemical treatment of wastewater, the use of hydrogen peroxide has gained much popularity. H_2O_2 is a powerful oxidizer that looks like water in its appearance, chemical formula and reaction products. Interestingly, it is versatile oxidant which is both safe and effective. It is one of the most powerful oxidizer known, stronger than chlorine, chlorine dioxide and potassium permanganate. Hence, the objective of this work is to investigate the effect of sulfide concentration, H_2O_2 dosage and reaction time on the removal of sulfide from petroleum refinery wastewater.

2. Materials and methods

2.1 Chemicals

The notable chemicals used in this study includes sulfide reagent 1 and 2 which contain potassium dichromate ($K_2Cr_2O_7$) and barium sulfate ($BaSO_4$) respectively for sulfides (S^{-2}) concentration determination. SulfaVer 4 reagent powder pillows which contains barium chloride (BaCl2) was used for determination of sulfate (SO_4^{-2}) concentration. High Range (HR) COD Digestion Vials which contain strong oxidizing agent, potassium dichromate ($K_2Cr_2O_7$) was used for Chemical Oxygen Demand (COD) concentration determination. Sodium sulphide ($Na_2S.9H_2O$) was used for sulfide simulated wastewater preparation. The chemical used for the oxidation procedure is hydrogen peroxide (H_2O_2) with concentration of 30%.

2.2 Actual wastewater

The actual wastewater samples that contain spent caustic was obtained from petroleum refinery industry in the East Coast region of Malaysia. The wastewater samples were collected in a glass bottle and are stored in cold storage at 4 °C for conservation [11]. The spent caustic wastewater is shown in figure 1.

Figure 1. Spent caustic wastewater.

2.3 Preparation of sulfide simulated wastewater

The sulfide simulated wastewater was prepared By adding 7.49 g sodium sulphate ($Na_2S.9H_2O$) into 1 L distilled water with 1000 mg/L of sulfide simulated wastewater concentration. Thereafter, the sulfide simulated wastewater was divided into five portions of equal volume (200 ml) with different sulfide simulated wastewater concentration (100 mg/L, 300 mg/L, 500 mg/L, 800 mg/L and 1000 mg/L) [12]. Prior to treatment, the sulfide concentration, sulfate concentration and pH of each portions was analyzed. The sulfide simulated wastewater is shown in figure 2.

Figure 2. Sulfide simulated wastewater.

2.4 Analysis of sulfide simulated wastewater and actual wastewater

There are three analysis which were carried out in this study. These includes the determination of sulfide (S^{-2}) concentration, sulfate (SO_4^{-2}) concentration and pH in sulfide simulated wastewater. The other wastewater parameter which is Chemical Oxygen Demand (COD) concentration in the actual petroleum refinery wastewater was also analyzed. The analysis of the samples was carried out twice that is before and after treatment.

2.4.1 Sulfide (S^{-2}) concentration. Sulfide (S^{-2}) concentrations of the samples were analyzed by using methylene blue method. The HACH spectrophotometer DR2800 type was used for this purpose, with the aid of sulfide reagent 1 and 2. Samples were diluted to ensure the sulfide concentration of effluents can be determined within the range, which is 0.005-0.8 mg/L. The sulfide concentration of the diluted samples is then multiplied by the dilution factor to obtain the actual sulfide concentration of the original sample. The dilution factor equation is presented in equation (1) as follow:

$$Dilution\ Factor = \frac{Final\ Volume\ (ml)}{Sample\ Volume\ (ml)} \quad (1)$$

2.4.2 Sulfate (SO_4^{-2}). Sulfate (SO_4^{-2}) concentration of the samples was analysed by using SulfaVer 4 method with the help of a DR2800 type spectrophotometer, with powder pillows reagent.

2.4.3 Chemical Oxygen Demand (COD) concentration. COD concentrations of the actual wastewater are analyzed by using a DR2800 type HACH spectrophotometer, with the aid of High Range (HR) Cod Digestion Reagent Vial HR that can measure up to 15 000 mg/L COD concentration and are heated in the HACH COD Digestion Reactor (DRB-200). The samples were diluted to ensure that the COD concentration of spent caustic wastewater can be determined within the range, which is 0-15 000 mg/L.

2.5 Oxidation method

The oxidation apparatus was set up to reduce sulfide concentration in sulfide simulated wastewater and actual wastewater by using strong oxidant, hydrogen peroxide (H_2O_2) with 30% purity [13]. Safety measures and precautions were taken into account when handling the strong oxidizing agent during sulfide removal. Specificaly, the experiments and the procedure was carried out in the fume hood. Figure 3 shows the experimental set up of the oxidation process. Three effects of operating condition on sulfide removal were investigated as presented in the subsequent subsections.

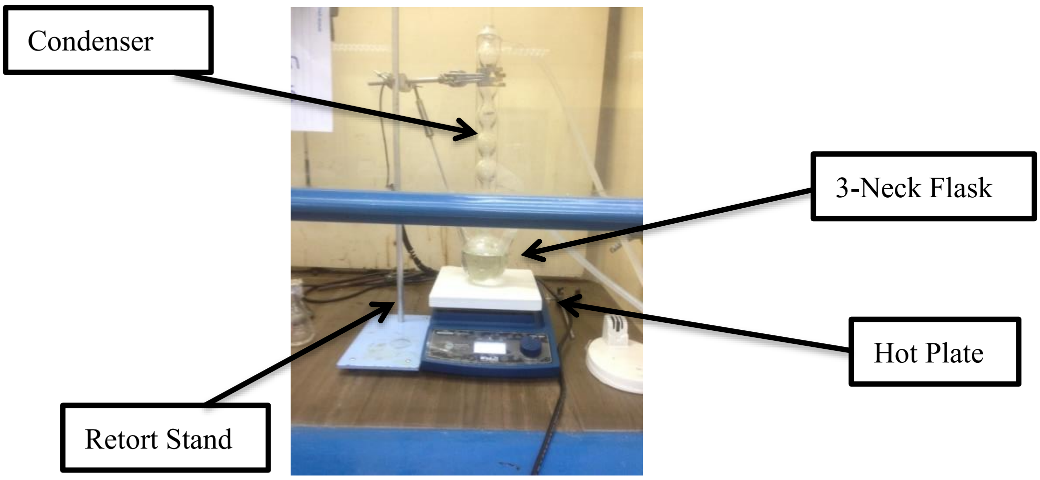

Figure 3. The experimental set up of the oxidation process.

2.5.1 Effect of concentration of sulfide simulated wastewater on sulfide removal. Five portions of sulfide simulated wastewater samples with different concentration (100 mg/L, 300 mg/L, 500 mg/L, 800 mg/L and 1000 mg/L) in equal volume (200 ml) were prepared [12]. Each portion was treated by constant hydrogen peroxide (H_2O_2) dosage of 1 ml. The experiment was run for constant time of 30 min [13], at constant temperature of 30 °C [14], constant agitation of 100 rpm and at a solution pH equal to 12. After treatment, the sulfide concentration, sulfate concentration and pH of each portion was analyzed.

2.5.2 Effect of hydrogen peroxide (H_2O_2) dosage on sulfide removal. The best concentration of sulfide simulated wastewater was selected to be used to study the effect of H_2O_2 dosage on sulfide removal. Hence, the hydrogen peroxide (H_2O_2) dosage was varied (0.25 ml, 0.5 ml, 1.0 ml, 1.5 ml and 2.5 ml) [15]. The experiment was run for constant time of 30 min [13], at a constant temperature of 30 °C [14], constant agitation of 100 rpm and at a solution pH equal to 12. After treatment, the sulfide concentration, sulfate concentration and pH of each portion was analyzed.

2.5.3 Effect of reaction time on sulfide removal. The best concentration of sulfide simulated wastewater and hydrogen peroxide (H_2O_2) dosage were taken to study the effect of reaction time on sulfide removal. The reaction time was varied between 10 min, 20 min, 30 min, 40 min, and 50 min at a constant temperature of 30 °C [14], constant agitation of 100 rpm and at a solution pH equal to 12. After treatment, the sulfide concentration, sulfate concentration and pH of each portion was analyzed.

2.6 Effect of best sulfide concentration, H_2O_2 dosage and reaction time on sulfide removal from actual wastewater

The best concentration of sulfide simulated wastewater (300 mg/L), H_2O_2 dosage (1.5 ml) and reaction time (30 min) were used to determine the percentage of sulfide removal from spent caustic wastewater. After treatment, the sulfide concentration, COD concentration and pH of the treated wastewater were analyzed.

3. Results and discussion

3.1. Characteristic of untreated spent caustic

The Sulfide (S^{-2}) concentration, Chemical Oxygen Demand (COD) concentration, and pH of untreated actual petroleum refinery wastewater samples were determined. The observable characteristic of the untreated spent caustic wastewater used in this study was compared with a previous study. The comparison, alongside the acceptable limit based on regulation is presented in table 1.

Table 1. Characteristics of untreated spent caustic wastewater.

Characteristic	This study	[3]	"Environment Quality Act 1974:Environment Quality (Sewage &Industrial Effluents) Regulations 1979" (2012) Standard B
Sulfide (S^{-2}), mg/L	51,400	34,517	0.50
Chemical Oxygen Demand (COD), mg/L	50,400	72,450	100
pH	13.00	12.97	5.5 – 9.0

As presented in table 1, it can be seen that the untreated spent caustic have high sulfide concentration, COD concentration and pH value which have exceeded the limit of DOE standard B regulations. It is worthy of note that there is a variation in sulfide concentration, COD concentration, and pH of the untreated spent caustic herein compared to previous study as presented in table 1. This may be attributed to the possible different operating conditions in the refinery plant from which the samples were collected. However, it can be concluded that the untreated spent caustic in this study and previous study, have high sulfide and COD concentration and have high pH value. This is not unusual as wastewater that contains spent caustic is expected to have high sulfide concentration which is known as strong oxidant. In addition to this, other chemicals such as cresylic acid, mercaptans, and sodium salts of napthenic are also commonly present [2]. According to [10], sulfide has a high oxygen demand of 2 mol O_2/L mol S^{2-} thus contributing significantly to oxygen depletion [3]. In another study [16], it was stated that the high COD concentration in untreated spent caustic may be attributed to the formation of elemental sulfur, resulting in high concentrations of sulfur compounds in the untreated spent caustic. On the other hand, the high pH of the untreated spent was attributed to the fact that the spent caustic is mainly based on caustic soda, otherwise known as sodium hydroxide which is highly alkaline in nature. Similarly, the spent caustic have high turbidity which contributes to the brown color of untreated spent caustic which is shown in figure 1.

From Figure 1, it is evident that the untreated spent caustic wastewater sample is brownish in color. In addition to this, it has an unpleasant smell. On the other hand, table 1 shows that the untreated spent caustic have high sulfide concentration, COD concentration and pH value that exceeds the limit of Malaysia's Department of Environment (DOE) regulations for standard B. Based on these, sulfide needs to be removed from spent caustic and its COD concentration and pH needs to be reduced before being released into water bodies. In this study suggest especially to remove sulfide concentration from spent caustic via oxidation method by using hydrogen peroxide (H_2O_2) alone which can bring harmful to human and environment.

3.2. Effect of sulfide concentration of simulated wastewater on sulfide removal

Oxidation method by using strong oxidant which is hydrogen peroxide H_2O_2 was used to reduce sulfide concentration in untreated spent caustic that specifically comes from the KTU tank. Therefore, H_2O_2 was used to remove sulfide concentration in sulfide simulated wastewater and obtain the best concentration, H_2O_2 dosage and reaction time that achieve highest percentages of sulfide concentration removal. Firstly, effect of sulphide concentration of simulated wastewater on sulfide removal was studied and the result is illustrated in figure 4.

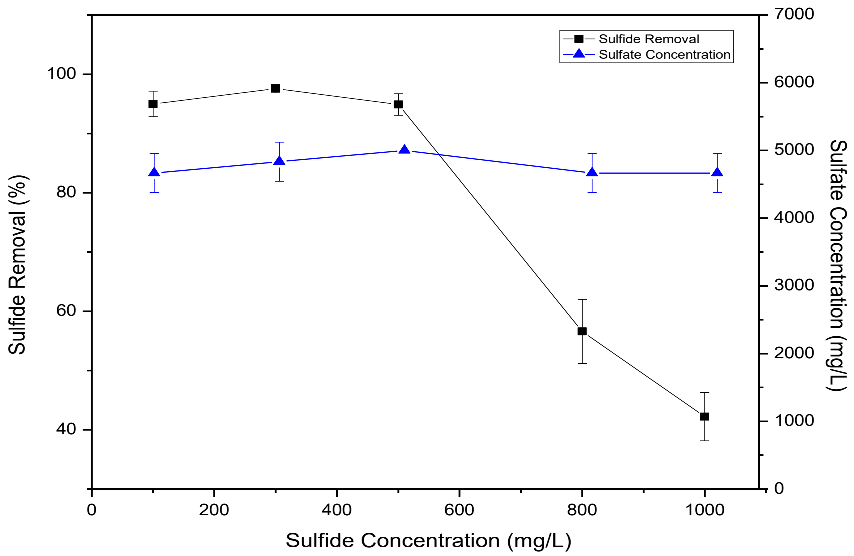

Figure 4. Effect of sulfide concentration of simulated wastewater on sulfide removal.

Figure 4 shows the plot of sulfide removal and sulfate concentration versus sulfide concentration. The study was performed using sulfide simulated wastewater of different sulfide concentration (100 mg/L, 300 mg/L, 500 mg/L, 800 mg/L and 1000 mg/L). The dosage of hydrogen peroxide (H_2O_2) was fixed at 1.0 ml hydrogen peroxide (H_2O_2) wherea the pH of the sulfide simulated wastewater is 12. The other experiment conditions which have been used for the oxidation process are as follows: temperature of 30 °C, agitation of 100 rpm and reaction time 30 min. From figure 4, it is evident that in the absence of H_2O_2 the sulfide concentration in simulated wastewater was high and there is a fluctualtion in the percentage of sulfide removal. Specfically, the sulfide removal was 95.0%, 97.6%, 94.9%, 56.5%, and 42.2% at 100, 300, 500, 800, and 1000 mg/L, respectively. Obviously, the best concentration of sulfide simulated wastewater with the highest percentage of sulfide removal (97.7%) is the sulfide simulated wastewater with sulfide concentration of 300 mg/L. This could be due to the generation of active form of oxidant, probably the hydroxyl radicals (OH•) and perhydroxyl (HO$_2$•) from the decomposition H_2O_2 at this point [15]. On the other hand, sulfate (SO_4^{-2}) concentration can be seen to increase as H_2O_2 was added with a simultaneous diminution of sulfide concentration in the samples. From Figure 4, the highest sulfate concentration is 5000 mg/L at 500 mg/L of sulfide concentration.

3.3. Effect of hydrogen peroxide (H_2O_2) dosage on sulfide removal

The effect of hydrogen peroxide (H_2O_2) dosage on sulfide removal is illustrated in figure 5 which shows the percentage of sulfide removal and sulfate concentration versus hydrogen peroxide (H_2O_2) dosage. Five different dosages of H_2O_2 (0.25 ml, 0.5 ml, 1.0 ml, 1.5 ml and 2.5 ml) were studied at the best concentration of sulfide simulated wastewater (300 mg/L). The pH of the sulfide simulated wastewater remain 12, and the experimental temperature is 30 °C, agitation of 100 rpm and reaction time is 30.

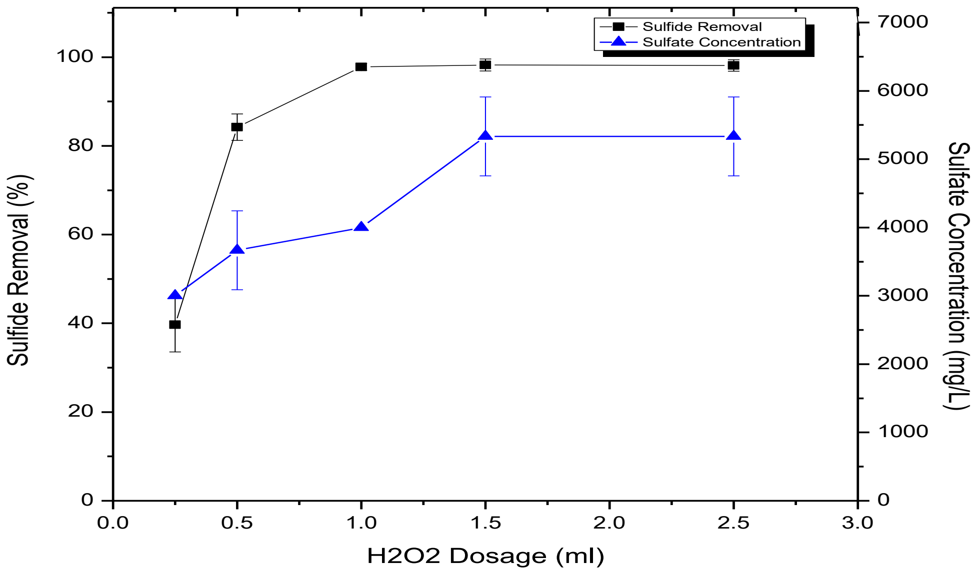

Figure 5. Effect of hydrogen peroxide (H_2O_2) dosage on sulfide removal.

As can be seen in figure 5, there is an initial increase in the percentage of sulfide removal which reached a maximum point at 1.5 ml as the dosage kept increasing. As presented in the figure, it is obvious that the sulfide removal was 39.6%, 84.2%, 97.7%, 98.2% and 98.1% at 0.25 ml, 0.5 ml, 1.0 ml, 1.5 ml and 2.5 ml, respectively. Hence, the best dosage of H_2O_2 which offered the highest percentage of sulfide removal (98.2%) is 1.5 ml dosage of H_2O_2 in the sulfide simulated wastewater. Therefore, it can be inferred that the 1.5 ml dosage is the optimal dosage required to eliminate the majority of product risk [15]. Based on the pH of sulfide simulated wastewater, the oxidation of these compounds by H_2O_2 gives sulfate ions or colloidal sulfur. This is believed to be the reason for the observable highest sulfate concentration of 5000 mg/L at 1.5 ml of H_2O_2 dosage as shown in figure 5.

3.4. Effect of reaction time on sulfide removal

Reaction time has an important role in the oxidation process. Figure 6 indicates the influence of reaction time on percentage sulfide removal and sulfate concentration. The reaction time (10 min, 20 min, 30 min, 40 min and 50 min) were investigated at the best concentration of sulfide simulated wastewater, 300 mg/L, with the best hydrogen peroxide (H_2O_2) dosage, 1.5 ml. During this oxidation process, the pH of sulfide simulated wastewater was fixed at 12, at a temperature of 30 °C and agitation of 100 rpm.

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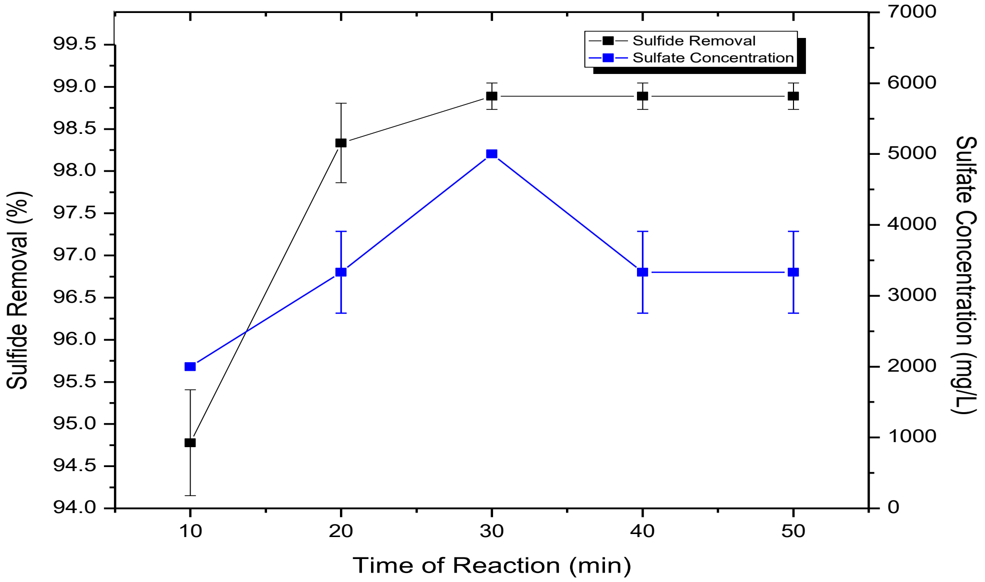

Figure 6. Effect of reaction time on sulfide removal.

As can be seen the result presented in Figure 6 showed an initial significant increase in sulfide removal which reached full equilibrium after a while despite the further increases in reaction time. Specifically, the best reaction time which produced the highest percentage sulfide removal of 98.8% is 30 min of reaction time in oxidation process. Notably, the use of hydrogen peroxide is particularly efficient for sulfide removal as the sulfide concentration has been significantly reduced just within 30 min of oxidation. Obviousy, the time seems to be very short to reach the equilibrium and this could probably be accrued to enhanced oxidation of the organic matter in the wastewater [15]. This is an indication that the activation by the hydrogen peroxide was largely efficient. As preented in Figure 6, the sulfide removal from sulfide simulated wastewater was 95.1%, 98.3%, 98.8%, 98.8% and 98.8% at 10 min, 20 min, 30 min, 40 min and 50 min, respectively. On the other hand, the highest sulfate concentration is 5000 mg/L at 30 min of reaction time.

3.5. Characteristics of treated spent caustic wastewater

The Sulfide (S^{-2}) concentration, Chemical Oxygen Demand (COD) concentration, and pH of actual petroleum refinery wastewater samples after oxidation process by using the best concentration of sulfide simulated wastewater (300 mg/L), H_2O_2 dosage (1.5 ml) and reaction time (30 min) were determined. Table 2 shows the characteristics of the treated spent caustic wastewater in this study and as compared with DOE standard B regulation.

Table 2. Characteristics of treated spent caustic wastewater.

Characteristic	This study	"Environment Quality Act 1974:Environment Quality (Sewage &Industrial Effluents) Regulations 1979" (2012) Standard B
Sulfide (S^{-2}), mg/L	0.5	0.50
Chemical Oxygen Demand (COD), mg/L	70	100
pH	8.41	5.5 – 9.0

As presented in table 2, it can be seen that sulfide (S^{-2}) concentration, chemical oxygen demand (COD) concentration and pH value of the treated spent caustic wastewater are 0.5 mg/L, 70 mg/L and 8.41 respectively. Interestingly, these values does meet the requirement of Department of Environment (DOE) for standard B which are 0.5 mg/L, 100 mg/L and 5.5 – 9.0, respectively. The percentages of sulfide, COD and pH reduction during three repetitive test times on the actual spent caustic wastewater is shown in figure 7.

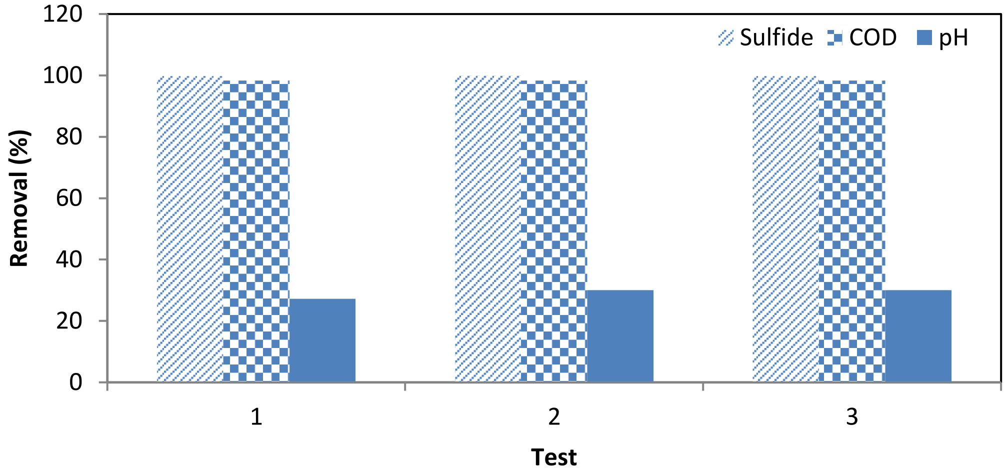

Figure 7. Percentages of sulfide, COD and pH removal in actual spent caustic wastewater.

The result in figure 7 shows the percentages of sulfide, COD, pH removal in actual spent caustic wastewater by using the best concentration of sulfide simulated wastewater, dosage hydrogen peroxide (H_2O_2) and reaction time which are 300 mg/L, 1.5 ml and 30 min, respectively. As can be seen in Figure 7, the average sulfide removal percentage from actual wastewater is 99.83% (0.5 mg/L) from 300 mg/L. This is possibly because H_2O_2 can be converted into hydroxyl radical (OH^-) which would therefore facilitate the diminution of sulfide (S^{-2}), while increasing the concentration of sulfates (SO_4^{-2}) in wastewater according to Equation 2.

$$S^{-2} + 4H_2O_2 \rightarrow SO_4^{-2} + 4H_2O \quad (2)$$

Besides that, Chemical Oxygen Demand (COD) concentration also reveals significant higher percentage removal from the wastewater which is 98.29% (70 mg/L) from 4100 mg/L. This indicates that hydrogen peroxide was also efficient for COD removal in spent caustic wastewater. Moreover, it shows that the organic matter in the wastewater was easily oxidized following the incorporation of hydrogen peroxide. In addition, the higher COD removal suggests that more hydroxyl radicals are being generated. On the other hand, pH value is also important in this study. Notably, the percentage pH reduction is 29.08% (8.41) from 11.83. In the case of the untreated spent caustic wastewater, it was originally highly alkaline. When hydrogen peroxide was added, the pH decreased and attained a lower pH in range of 5.5 – 9.0 which conforms with the DOE requirement for standard B.

4 Conclusion

The reduction of sulfide (S^{-2}) concentration from sulfide simulated wastewater via oxidation method by using strong oxidant hydrogen peroxide (H_2O_2) is presented herein. Result shows that the best concentration of sulfide simulated wastewater (300 mg/L), H_2O_2 dosage (1.5 ml) and reaction time (30 min) was able to reduce 97.67%, 98.22% and 98.89% sulfide concentration from sulfide simulated wastewater. Thus, sulfide removal from the actual petroleum refinery wastewater which is spent caustic

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by using H_2O_2 was able to reduce 99.83% (0.5 mg/L) sulfide concentration. Besides that, Chemical Oxygen Demand (COD) concentration was reduced by 98.29% (70 mg/L) and pH became 8.41 after treatment. The treated spent caustic does meets the DOE requirement standard B for sulfide concentration (0.5 mg/L), COD concentration (100 mg/L) and pH (5.5 – 9.0). Therefore, oxidation method by using strong oxidant hydrogen peroxide alone in removal sulfide as well as for COD and pH is an effective method. This method offers an interesting treatment for spent caustic, as it an effective, environmentally safe and easy approach compared to other treatment methods such as biological processes.

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