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Sulphide pollutants elimination and degradation in petroleum wastewater by ozonation process

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Abstract: An efficient and robust chemical oxidation process using an OZ-3G ozone generator was developed and investigated to degrade and reduce sulphide toxicity in petrochemical wastewater. Different concentrations of sulphide in synthetic wastewater were prepared and evaluated using the Spectrophotometric technique. The values of Chemical Oxygen Demand (COD) and pH were also studied. The obtained results demonstrated that 100 minutes of ozone treatment removed 97.4 % for 40 mg/L concentration. The pH was decreased gradually with the increase along the time of oxidation. Based on the ozone method's significant results, ozonation can be considered a potential candidate method for wastewater treatment in petroleum refineries.
Keywords: COD, Ozone Treatment, Sulphide pollutants, Wastewater.

1. Introduction

Studying new desulphurization processes is the key to bring more profit to the oil refining companies [1]. Hydrogen sulphide (H_2S) is a highly toxic pollutant and a corrosive chemical with the characteristic foul odour of rotten eggs, that is highly employed in food processing plants, breweries, petrochemical industry, oil fields, nuclear power plants, sewage, and many industrial entities [2-4]. The removal of dissolved sulphide (sulphide in an aqueous phase) is necessary to protect the environment and confirm human safety regulations. It is considered one of the most significant hazardous pollutants discharged into the wastewater effluent from crude oil refineries and other resources [5].

Many techniques have been established for this purpose, such as coagulation, adsorption, biological degradation, and electrochemical oxidation [3-6]. Autotrophic denitrification was utilized to remove dissolved H_2S from oil-refining wastewater studied by Vaiopoulou and his group [7]. Multi-stage biological technique attained approximately a complete removal of H_2S with a 70 % reduction of the energy required for the compression of CO_2. Another study demonstrated electrochemical oxidation to remove H_2S by converting it to sulphate and thiosulphate using a perpendicular electrochemical reactor with vitreous carbon anode [8].

Kanjanarong *et al.* [9] reported using biochar to remove H_2S by using a column packed integrated with a bench-scale continuous-stirred tank reactor. The obtained results showed that the biochar was efficient for removing H_2S (approximately 98%) via sorption, chemical bonding and active functional group. Although these techniques achieve good performance towards the purification of wastewater, they still suffer from some drawbacks, including high cost, unsuitability to operate in large scale operations and inefficiency in industrial wastewater treatment [10]. Oxidation of wastewater via advanced oxidation processes, including UV/H_2O_2, TiO_2/UV, and Fenton's regent oxidation has gained much attention due to its simplicity and ability to improve the removal of contaminants from wastewater

[11-13]. Among these methods, chemical oxidation via ozonation has recently been in the limelight as a suitable tool in wastewater treatment due to its ability to oxidize many complex inorganic and efficiencies in removal of colour as compared with other well-established oxidizers such as chlorine, potassium permanganate, and hydrogen peroxide [14-15]. Ozonation is more potent than photocatalysis in organic degradation and more ascendant in treating highly concentrated samples.

Herein, chemical oxidation of wastewater effluent taken from Al-Daura refinery, Iraq has been investigated to remove sulphide (S^{2-}), by employing ozone treatment. COD and pH were also examined. The presented results show that the ozonation process attains significant contaminant removal.

2.   Materials and Methods

Analytical grade sodium sulphide ($Na_2S.9H_2O$) (purchased from Sigma-Aldrich) was used without any purification. Petrochemical wastewater effluent was collected from Al-Daura refinery, Iraq. The characteristics of petrochemical wastewater collected from Al-Daura refinery is Table 1. This wastewater effluent contains initial sulphide concentrations of 0.0028 mg/L, with a pH (12.65) and COD values of 524 mg/L, respectively. For comparison purpose, synthetic sulphide samples of hydrogen sulphide (H_2S) solution were prepared in the lab with three different concentrations of 20, 30, and 40 mg/L by dissolving (0.15, 0.225, 0.3) gm of ($Na_2S.9H_2O$) in 1L of distilled water individually.

Table 1: Characteristics of Al-Daura refinery wastewater

Parameter	Sulphide concentrations mg/L	pH	COD mg/L
Value	0.0028	12.65	524

Ozone was generated using an OZ-3G generator (china) under dry air and the oxygen flow rate of 6 L/min with ozone consistency of 50%, in 1 L sulphide solution. In this work, three different concentrations of sulphide were conducted for synthetic wastewater by dissolving 0.15, 0.225, and 0.3 g of sodium sulphide in 1 L of deionized water to obtain 20, 30, and 40 mg/L concentrations, respectively. Sulphide samples were examined under ozone exposure for 100 minutes with an increment of 20 minutes. On the other hand, actual wastewater was also utilized where the sulphide concentration was calculated to be approximately 0.0028 mg/L with pH and COD of 12.65 and 532 mg/L, respectively. Sulphide concentrations of 20 and 40 mg/L were prepared for the actual petrochemical wastewater by dissolving 0.15 g and 0.3 g of $Na_2S.9H_2O$ in 1 L of petrochemical wastewater, respectively.

The resulting sulphide concentrations were measured via a portable digital spectrophotometer (HACH-DR2800, USA), set at 690 nm wavelength used to calculate the electromagnetic waves absorbance of each sample. The weight of sodium sulphide was calculated following the formula in Eqs. (1) and (2) [16]:

$$Number\ of\ moles\ of\ atoms = \frac{mass\ in\ gram}{molar\ mass\ of\ atoms} \tag{1}$$

$$Wt_\circ = M \times V \times M.Wt_\circ \tag{2}$$

Where $Wt_\circ$ and $M.Wt_\circ$ represent the weight (g/L) and the molecular weight of $Na_2S.9H_2O$, respectively. *M* is the number of moles of sulphide in g/L, and *V* represents the solution's volume.

The pH of the resulted sulphide samples of synthetic and actual wastewater have been determined by using Mettler Toledo, USA pH meter. Besides, COD was obtained from the sulphide samples of actual wastewater using Hach-DR2800, USA portable digital spectrophotometer of wavelength set at 439 nm. The removal efficiency (% Removal) of COD was calculated as represented in Eq. (3) [17]:

$$\%\ Removal = \frac{C_\circ - C}{C_\circ} \times 100 \tag{3}$$

Co and C are the initial and different COD concentrations at a time (t), respectively.

3.   Results and Discussion

Figure 1a shows the sulphide concentrations of the synthetic wastewater under 100 minutes of ozone exposure. After 60 minutes, a noticeable drop in sulphide concentration was observed.

The concentrations were found to be slightly fluctuating between 2.36 and 1.8 mg/L for the initially employed concentrations. For clarification, the results obtained for the sulphide concentration of 40 mg/L upon exposure to ozone for 60 minutes is demonstrated in Figure 1 (b).

From the figure, the sulphide concentration was dropped to 21.56 mg/L in the first 5 minutes while it decreases to 4.35 mg/L concentration after 10 minutes of ozone exposure. Because in an aqueous solution, ozone reacts with hydrogen sulphide in two competing simultaneous reactions, one to produce elemental sulphur, and one to produce sulphuric acid.
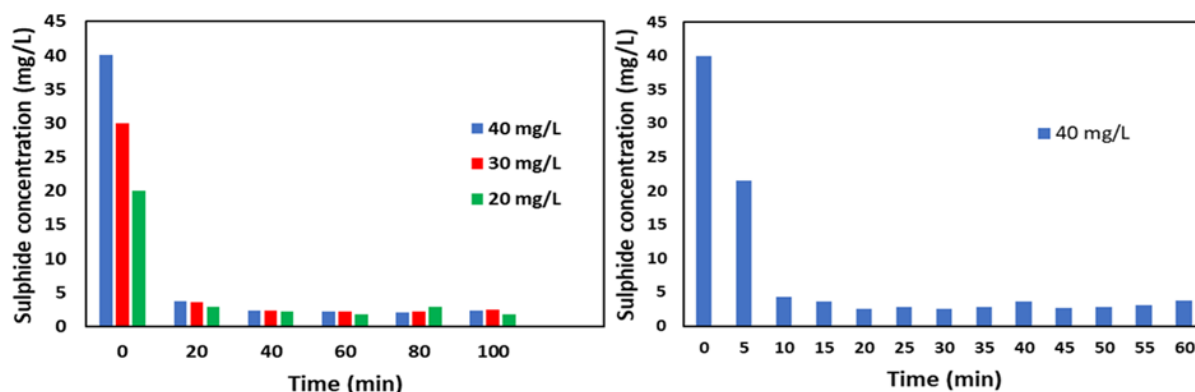
Figure 1: (a) Sulphide concentrations of synthetic wastewater samples upon exposure to 100 min of ozone. (b) Sulphide concentrations over 60 min of ozone exposure

For the remaining 50 minutes of treatment, the concentration keeps changing between 3.73   2.55 mg/L. Thus, the oxidant of S^{2-} in the form of sulphates (SO_{4-2}) is within the first 15 min of the Ozonation process. After 100 minutes of ozonation, the removal of sulphide (S^{2-}) in the form of sulphates (SO_{4-2}) was calculated to be 97.21, 95.65, and 91.72%. While sulphide concentrations were 40, 30 and 20 mg/L, respectively.

Initially, the pH was approximately 10. However, after the concentration drop, the pH was calculated to be less than four because of sulphate (SO_4^{-2}) presence in the form of sulphuric acid, as shown in Figure 2, for comparison purpose, a similar procedure conducted to the synthetic samples was applied to the actual wastewater samples where S^{-2} concentrations measured every 20 minutes.
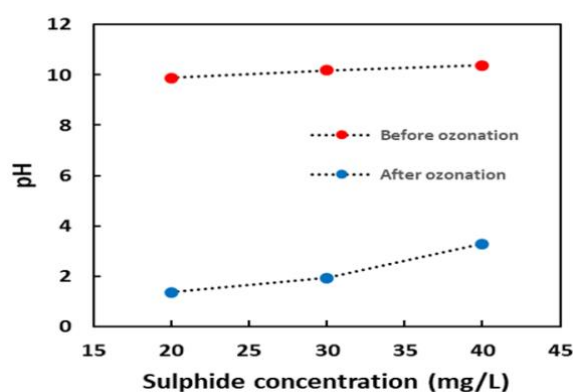
Figure 2: Sulphide concentrations (20, 30, and 40 mg/L) vs pH before and after Ozonation.

Figure 3 (a) and (b) demonstrates that the S^{-2} concentration of the actual wastewater attained almost the same synthetic wastewater behaviour after exposing the samples to ozone for 100 minutes and 60 minutes, respectively. The sulphide removal was calculated to be frequently fluctuating between 3.75 mg/L and 2.48 mg/L, under 100 minutes of ozone exposure.
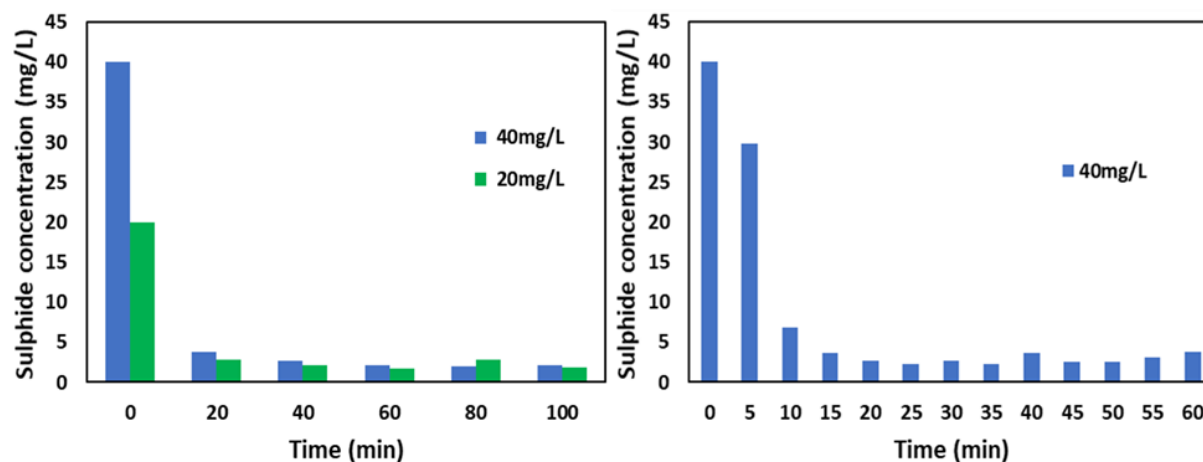
Figure 3: (a) Sulphide concentrations (20 and 40 mg/L) under 100 min of ozonation and (b) 40 mg/L

The removal efficiency was 97.21 and 91.73% of petrochemical wastewater of S^{-2} concentration of 40 and 20 mg/L, respectively. For the actual petrochemical wastewater, the pH values were 12.1 and 12.41 for 20 and 40 mg/L sulphide concentrations.

Figure 4 shows the impact of ozonation on the pH of the proposed synthetic wastewater samples (20, 30, and 40 mg/L). As can be seen, the pH values decrease proportionally with the increase in the ozonation time. This can be mainly attributed to the oxidation and conversion of S^{2-} to SO_4^{2-}, as explained in Eq. 4 [18]:

$$H_2S + 2O_2 \rightarrow H_2SO_4 \tag{4}$$

During the Ozonation process, exposure to 100 minutes of ozone attained to decrease pH from 10.42, 10.19, and 9.88 to 3.96, 1.85 and 1.66, respectively, for 40, 30, and 20 mg/L sulphide concentration in synthetic wastewater. In contrast, the effect of ozonation on pH was not obvious in petrochemical wastewater samples due to alkaline components in the wastewater sample which indicates the power to react with SO_4^{-2} and resist changing PH of the actual sample solution.
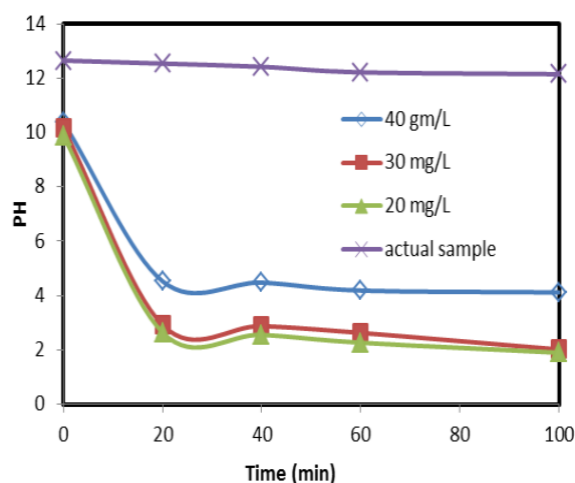

Figure 4: pH Levels as a function of time for synthetic wastewater samples (20, 30, and 40 mg/L) and actual sample

Initially, for the 40 mg/L petrochemical wastewater sample, the COD concentration was found to be 668 mg/L. After 100 min of ozonation, the COD value decreased about five times to be 75 mg/L with a removal efficiency of 88.4 % (Figure 5). Furthermore, the initial COD concentration was 564 mg/L in

the 20 mg/L actual samples, which decreased after 100 min of ozone exposure to be 101 mg/L with a removal efficiency of 82.8 %.

The results reported in this work agrees with a previous result published by (Yang *et al.* (2002), Jinlan *et.al.*, (2016), Galdeano *et al.* (2018) and Xiaoning and Rui (2019) [19-22].
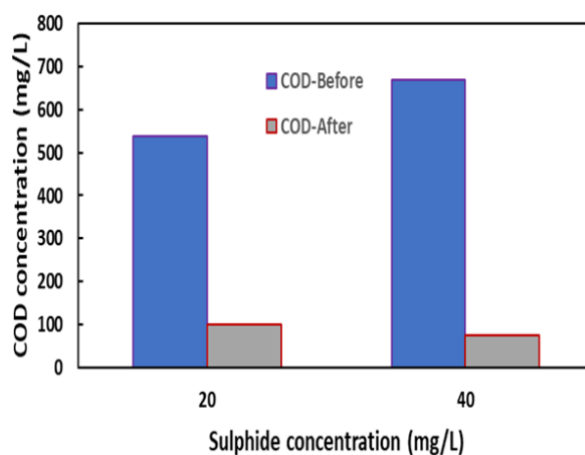
Figure 5: COD concentrations of actual wastewater samples (20 and 40 mg/L) before and after ozonation

4.   Conclusions

A comparative study was conducted between synthetic and actual wastewater to study sulphide removal efficiency, COD values, and the effect of the ozonation process on pH. For the actual wastewater samples, S^{-2} concentrations demonstrated the same behaviour as the synthetic wastewater during the ozonation process. The removal efficiency of sulphide was approximately 97% for both actual and synthetic wastewater samples of 40 mg/L after 100 minutes of ozonation. Petrochemical wastewater samples showed no noticeable impact on pH values upon exposure to ozone due to the alkaline component contained in the petrochemical wastewater sample. The initial values of pH were higher than 9 and 12 for synthetic and actual wastewater samples, respectively. COD values were also observed to be reduced to 80% in all the samples. Based on the aforementioned results, ozone treatment can be an effective way for wastewater contaminant removal in petrochemical applications with significant control of COD concentrations.

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