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Sulphide removal from petroleum refinery wastewaters by catalytic oxidation

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ABSTRACT

The catalytic oxidation of sulphides present in oil refinery wastewaters was investigated in the present study. The wastewaters were obtained from the wastewater treatment plant of the oil refinery in Matosinhos (Portugal), *Galp Energia*. Air, NaOCl and H_2O_2 were chosen as oxidants and Fe^{3+} and Mn^{2+} as the two catalysts to assess the effective combination of catalyst–oxidant for sulphide removal after oil separation in parallel plate interceptors. Primarily, air (oxygen) was used as the oxidant and the efficiency of two catalysts (Fe^{3+} and Mn^{2+}) for sulphide removal was evaluated. Experimental data suggested that Fe^{3+} catalysed sulphide removal in the presence of oxygen was more effective than Mn^{2+} catalysed reaction. In a subsequent study, oxygen was replaced by NaOCl and H_2O_2, and the potential of various catalyst–oxidant combinations, $NaOCl + [Fe^{3+}]$, $NaOCl + [Mn^{2+}]$, $H_2O_2 + [Fe^{3+}]$, $H_2O_2 + [Mn^{2+}]$, was assessed. The $NaOCl + [Fe^{3+}]$ combination achieved the maximum sulphide oxidation. Pseudo-first-order and pseudo-second-order reaction models were fitted to the kinetic experimental data. The influence of temperature on the kinetic rate was also investigated.

Keywords: Oil refinery wastewater; Sulphide removal; Catalyst; Oxidation; Kinetics

1. Introduction

Refineries are potential contributors to groundwater and surface water contamination. Wastewater in the refineries is generally highly contaminated and arises from various processes (such as wastewater from desalting, water from cooling towers, stormwater, distillation or cracking). Oil refinery wastewater contains large quantities of emulsified oil, phenols, mercaptans, cyanides, nitrogen and sulphur, in the form of ammonia and hydrogen sulphide (H_2S), respectively, and other micropollutants [1–4]. The treatment of this kind of wastewater involves a sequence of unit operations (American Petroleum Institute [API] separator, parallel plate interceptor [PPI], oxidation of sulphides often coupled with chemical coagulation and flocculation, dissolved air flotation [DAF] and biological treatment).

Crude oil is termed as sweet or sour depending on the low or high sulphur content present in the oil, respectively. Due to the contact between oil and water at various stages of the refining operation, significant quantities of sulphur compounds enter the wastewater stream. Most of these sulphur compounds are sulphides, which are typically present in the wastewater as sulphide ions [5]. Sulphide as H_2S gas under anaerobic conditions is hazardous. The graveness of situation increases if the same wastewater is treated under aerobic conditions, when part of the air supplied will be utilized for oxidation of sulphide back to sulphate,

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which leads to reduced efficiency of the aerobic treatment. The released wastewater with high sulphate levels will be discharged into the environment, which is undesirable [6].

Corrosion is another major problem caused by the sulphide present in wastewaters released from refineries. Jacobs et al. [7] provided significant evidence about the increased copper corrosion problems in the presence of sulphide in water utilities causing rapid copper pitting tube failures. Sulphide concentration as low as 0.007 mg/L [8] is recognised as a major cause of copper corrosion. Dissolved free sulphides (H_2S, HS^- and S^{2-}) are also responsible for the corrosion of steel and stainless steel, apart from copper. Sulphides present in aqueous solution are responsible for stress corrosion cracking of steel, which is also called sulphide stress cracking.

H_2S, which is the most important form of sulphur exists in equilibrium with bisulphide (HS^-) and sulphide (S^{2-}) in aqueous solution and can volatilize as H_2S gas [9]. Sulphide being the most reduced form of sulphur, has a high oxygen demand ($2\,\mathrm{mol\,O_2\,L^{-1}\,mol^{-1}\,S^{2-}}$), causing the depletion of oxygen at the point of sourwater discharge. Researchers have found that oxidation of H_2S by oxygen progresses slowly and the process is feasible under pressurized conditions [10]. Transition metal ions and their complexes also enhance sulphur oxidation by oxygen [11].

Oxidation of H_2S is also a function of temperature, pH and ionic strength. The rate of H_2S oxidation is found to increase with increasing temperature and pH up to 8. Above pH 8, the rate is found to be independent of pH [12]. The rates of oxidation are even much higher in seawater than in air-saturated water. Biological processes are responsible for the oxidation of H_2S to ${SO_4}^{2-}$ or elemental sulphur in ventilated water wells [13]. Chemical reaction of sulphides with dissolved oxygen yields a number of products including hyposulphite ($S_2{O_3}^{2-}$), sulphate (${SO_4}^{2-}$), sulphite (${SO_3}^{2-}$) or sulphur as given in Eqs. (1)–(4) [14], but the process is slow and complex [15,16].

$$HS^- + \frac{1}{2}O_2 \rightarrow S^0 + OH^- \quad (1)$$

$$HS^- + O_2 \rightarrow \frac{1}{2}S_2O_3^{2-} + \frac{1}{2}H_2O \quad (2)$$

$$HS^- + \frac{3}{2}O_2 \rightarrow SO_3^{2-} + H^+ \quad (3)$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad (4)$$

The conventional and current technologies employed for sulphide removal mainly include the physicochemical processes involving the addition of various chemicals as oxidants [17], direct air stripping and chemical precipitation. Iron salts such as ferric chloride and ferrous sulphate have also been extensively used for sulphide precipitation in refinery wastewaters. Fe(II) removes the sulphide by precipitating it as ferrous sulphide (FeS). Fe(III) oxidizes sulphide to elemental sulphur while being reduced to Fe(II), which can subsequently produce FeS [18]. Although, complete removal of dissolved sulphide is difficult and an excess addition of iron salts is required to obtain adequate control [18]. Recently, an electrochemical approach has also been proposed for wastewater sulphide removal, in which sulphide can be directly oxidized at anode [19–21]. Biological oxidation of sulphide by means of nitrate reducing-sulphide oxidizing bacteria (NR-SOB) [22] has also shown promising results. But most of these techniques are not considered economical and have their own limitations like sludge generation [23]. The oxidation of sulphide to sulfur is preferable since this requires the least amount of electrons and thus less energy input is needed [19]. Several researchers have also performed the catalytic oxidation of sulphide using sulphur black dye [24], carbon black, $FeCl_3$ [25,26] and hydrogen peroxide [27] as catalysts.

In the present study, the removal of sulphide by catalytic oxidation was investigated. Fe(III) and Mn(II) were selected as catalysts and oxygen, NaOCl and H_2O_2 were used as oxidants. The reaction temperature was investigated to determine its effect on the reaction rate over the range of 293–313 K. The effect of contact time and concentration of catalysts were the two parameters studied to evaluate the performance of the overall process. The real wastewater samples were used in the study to determine the feasibility of using catalytic oxidation in treating the sulphide-containing wastewater from wastewater treatment plant (WWTP) of the refinery.

2. Materials and methods

2.1. WWTP samples

The wastewater was collected from the WWTP of the oil refinery in Matosinhos (Portugal), *Galp Energia*. The wastewater samples were taken from the effluents of PPI and sulphide oxidation/coagulation (OC) unit of WWTP. Detailed analyses of both samples were performed. The characteristics of the wastewater obtained upstream (effluent of PPI) and downstream from the OC unit are shown in Table 1. The wastewater from the PPIs showed high concentrations of sulphide, oil and grease, Total Petroleum Hydrocarbons (TPH) and organic matter (expressed as chemical oxygen demand [COD] and biochemical oxygen demand [BOD_5]). Total and volatile suspended solids are also significant, but pH is practically neutral. The wastewater samples used for the evaluation of the sulphide oxidation were collected after the PPI, at three different days.

2.2. Analytical methods

Total suspended solids (TSS), volatile suspended solids (VSS), COD, BOD_5, chloride and total nitrogen were measured according to Standard Methods (SM) for the Examination of Water and Wastewater [28]. Electrical conductivity and pH were measured using a pH/conductivity meter HANNA HI 4522. Oil and grease were analysed by the partition-gravimetric method (SM, method 5520-D) using an analytical balance (Denver Instrument Company, AA-200). TPH were analysed by the Soxhlet extraction method (SM, method 5520-F) using a spectrophotometer (UNICAM Helios α spectrophotometer). The detection limit for oil and grease was 0.5 mg L^{-1} and for TPH it was 0.1 mg L^{-1}. Phenols in the samples were measured and analysed by chloroform extraction and direct photometric methods [29]. Sulphide analysis was performed by the iodometric method (SM, method 4500-S^{2-} F) [28]. The detection limits for TSS, VSS, COD, BOD_5 and sulphide were 0.5 mg L^{-1}, 0.5 mg L^{-1}, 10 mg O_2 L^{-1}, 1 mg O_2 L^{-1} and 0.1 mg L^{-1}, respectively. All reagents used in the study were of analytical grade.

2.3. Experimental procedure

Oxygen from the air served as an oxidant and Fe^{3+} and Mn^{2+} acted as model catalysts for the catalytic oxidation of sulphide. The catalysts were added into four flasks containing 500 mL of wastewater samples. The sulphate salts of Fe^{3+} and Mn^{2+} were used to prepare the solutions having Fe^{3+} concentration ranging from 0.08 to 0.78 mg L^{-1} and Mn^{2+} concentration ranging from 0.04 to 0.54 mg L^{-1}. The prepared solutions were then aerated for 30 min using air diffusers. The tests were carried out at room temperature (± 20°C) and at pH 6.8. The concentration of sulphide in the samples was measured before and after the oxidation process. The sulphide concentration in the samples was 156 mg L^{-1} prior to the oxidation process.

The suitability of NaOCl and H_2O_2 as oxidants was also investigated using Fe^{3+} and Mn^{2+} as catalysts and the following combinations were checked for their performance: NaOCl + [Fe^{3+}], NaOCl + [Mn^{2+}], H_2O_2 + [Fe^{3+}], H_2O_2 + [Mn^{2+}]. The concentrations of Fe^{3+}, Mn^{2+}, NaOCl and H_2O_2 were 1.2, 1.0, 0.4–1.6 and 0.26–1.5 mg L^{-1}, respectively. The wastewater samples collected from WWTP contained high concentrations of suspended particles and therefore were vacuum filtered prior to the sulphide removal tests with the above oxidant–catalyst combination. The tests were conducted at 20°C and the pH was between 6.4 and 6.9 and the initial sulphide concentration was 148 mg L^{-1}.

2.4. Kinetics of sulphide removal

The kinetics of sulphide removal using Fe^{3+} as a catalyst in the presence of oxygen from the air was

Table 1
Physicochemical characteristics of the refinery wastewater upstream and downstream from sulphide oxidation unit

Parameters	PPIs	OC
pH	6.6	6.7
TSS (mg L^{-1})	1,446	1,130
VSS (mg L^{-1})	1,279	869
TPH (mg L^{-1})	909	631
Oil and grease (mg L^{-1})	1,479	789
COD (mg L^{-1})	1,095	595
BOD_5 (mg L^{-1})	532	295
Sulphides (mg L^{-1})	183	40
Total nitrogen (mg L^{-1})	125	93
Phenols (mg L^{-1})	1.2	1.0
Chlorides (mg L^{-1})	460	340
Electrical conductivity (mS cm^{-1})	1857	1,635

PPIs-Treated wastewater from PPIs unit; OC-Treated wastewater from coagulation and oxidation unit.

also studied. Experiments were performed by continuously bubbling air through the liquid phase. After regular time intervals up to 30 min, a fixed sample volume was collected for the determination of the reduction in sulphide concentration over time. The initial concentration of sulphide in the samples was found to be 161 mg L^{-1}.

2.5. Effect of temperature on sulphide removal

The experiments were also conducted at different temperatures, viz., 293, 298, 303 and 313 K, to examine the influence of temperature on the performance of the catalytic oxidation process.

2.6. Parameters estimation

The experimental data obtained from kinetic studies were fitted to mathematical models by a non-linear regression method (FigSys for Windows from BIOSOFT). Model parameters were obtained by minimizing the sum of the squared deviations between experimental and predicted values. Model goodness was evaluated through the calculation of relative standard deviations (RSD), sum of square residuals (S_2^R) and regression coefficient (R^2).

3. Results and discussion

3.1. Effect of catalyst type

Experiments were conducted to evaluate and compare the performance of Fe^{3+} and Mn^{2+} as catalysts for sulphide removal in the presence of oxygen from air. The catalytic oxidation was performed using Fe^{3+} and Mn^{2+} salts under identical experimental conditions. The characteristics of the wastewater sample were: pH = 6.8; $T = 20$℃ and $[S^{2-}]$ = 156 mg L^{-1}. The results (Fig. 1) suggest that the concentration of 1.5 mg L^{-1} Mn^{2+} is sufficient to achieve a 64% sulphide removal in the presence of oxygen, at room temperature. While, only 1.2 mg L^{-1} Fe^{3+} was necessary to achieve sulphide removal with an efficiency of 83%. A minimum concentration of 0.3 mg L^{-1} Fe^{3+} removed 40% of sulphide. However, the maximum removal efficiency of 90% was achieved using an Fe^{3+} concentration of 2.4 mg L^{-1}.

The better performance of Fe(III) as a catalyst for sulphide removal has been proven previously by other researchers [30]. Tomar and Abdullah [10] reported that the optimum iron dosage for complete sulphide removal was 20% lower for the ferric solution than the ferrous solution. The presence of O_2 or any weak oxidizing agent is also found to assist the formation of FeS_2 [31].

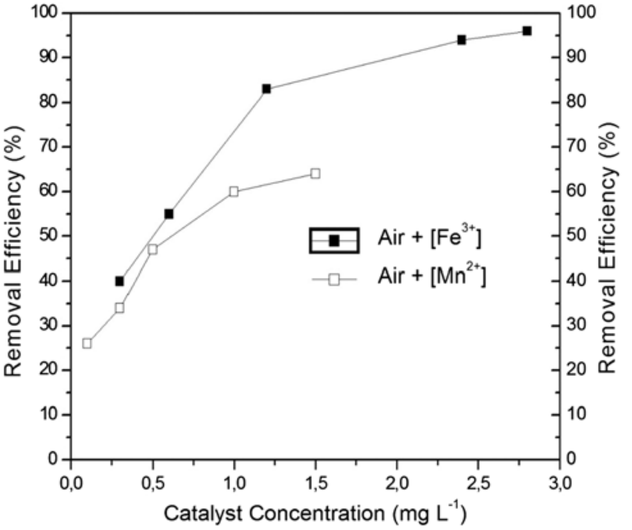

Fig. 1. Sulphide removal efficiency by catalytic oxidation with oxygen from air and Fe^{3+} and Mn^{2+} as catalysts ($[S^{2-}]_{initial} = 156$ mg L^{-1}; pH = 6.8; $T = 293$ K).

The net autooxidation stoichiometry of sulphide in the presence of iron (haematite) has been previously explained by Herszage and Afonso [32] as provided in Eqs. (5)–(8):

$$4Fe_2O_3 + H_2S + 14H^+ \rightarrow 8Fe_{aq}^{+2} + SO_4^{=} + 8H_2O \tag{5}$$

$$4Fe_2O_3 + 2H_2S + 14H^+ \rightarrow 8Fe_{aq}^{+2} + S_2O_3^{=} + 9H_2O \tag{6}$$

$$H_2S + 2O_2 \rightarrow SO_4^{=} + 2H^+ \tag{7}$$

$$2H_2S + 2O_2 \rightarrow S_2O_3^{=} + H_2O + 2H^+ \tag{8}$$

In the present investigation, wastewater samples, effluent from the sulphide oxidation and coagulation unit (catalyst dose: 4.5 mg L^{-1} of iron sulphate; oxidant: air; coagulant dose: 20 mg Al_2O_3 L^{-1} of PAX-18 (17% Al_2O_3); neutral pH; residence time = 4 min), were obtained during five monitoring surveys at the WWTP in different seasons of the year. The sulphide removal efficiency of the process varied from 74.1 to 80.4% in the presence of 4.5 mg L^{-1} $Fe_2(SO_4)_3$ and dissolved air. The lower efficiency observed in real conditions might be attributed to the variation in oxygen concentration and temperature of the wastewaters.

3.2. Effect of oxidant type

The corrosion caused by sulphide can be controlled by oxidizing sulphide with various oxidants such as hydrogen peroxide, hypochlorites, chlorine and potassium permanganate other than oxygen [10,33]. In the present study, the performance of the two other oxidants, namely NaOCl and H_2O_2, was examined and four combinations were evaluated: NaOCl + [Fe^{3+}], NaOCl + [Mn^{2+}], H_2O_2 + [Fe^{3+}], H_2O_2 + [Mn^{2+}]. The characteristics of the wastewater sample were: pH = 6.6; $T = 20$°C; [S^{2-}] = 148 mg L^{-1}. The removal of sulphide was significantly altered when replacing the air by these oxidants. The results in Fig. 2 exhibit that NaOCl + [Fe^{3+}] is a potential catalyst–oxidant combination for sulphide removal and a concentration of 1.6 mg L^{-1} NaOCl gives the maximum sulphide removal efficiency (*ca*. 93%). Cadena and Peters [34] also observed that chlorine compounds are relatively more efficient than H_2O_2 and O_2 for the oxidation of sulphide. As can be seen in Table 1, the sulphide concentration in the effluent of oxidation (OC) unit indicates that *ca*. 78% sulphide removal is achieved in WWTP, *Galp Energia*. Thus, the results of the present study suggest that the combination of NaOCl + [Fe^{3+}] can be considered as an effective catalyst–oxidant combination for sulphide removal from the oil refinery wastewaters.

3.3. Oxidation kinetics of sulphide removal

Sulphide oxidation can result in various end products, namely viz. S^0, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-} [14]. As the oxidation of sulphide using air or oxygen over NaOCl and H_2O_2 offers an alternative as well as an inexpensive means of treating wastewaters, the sulphide kinetics was conducted using O_2 from air and Fe^{3+} as a catalyst at 293 K. The progress of the reaction was noted by measuring the reduction in the sulphide concentration with time. The characteristics of the wastewater sample were: pH = 6.8; $T = 20$°C; [S^{2-}] = 161 mg L^{-1}. It was observed that sulphide concentration was reduced to nearly half in 10 min and it took 30 min to minimize the sulphide concentration to 0.00065 M (21 mg L^{-1}) from 0.005 M (160 mg L^{-1}) (Fig. 3). Ahmad et al. [35] also studied the oxidation kinetics of sulphide in the presence of H_2O_2 and ferric oxide catalyst and achieved complete removal of sulphide in 55 min when the initial sulphide concentration was 0.0128 M (410 mg L^{-1}).

Kinetic experiments were also conducted at 298, 303, 308 and 313 K to study the behaviour of sulphide oxidation on increasing the temperature. It was observed that with the increase in temperature, sulphide removal efficiency increased slightly. Similar results were obtained by Ahmad et al. [35].

3.3.1. Kinetic models

Two well-known kinetic models, viz., pseudo-first-order and pseudo-second-order models were fitted to the experimental data obtained from the kinetic studies. Pseudo-first-order and second-order kinetic models can be given as Eqs. (9) and (10):

$$C_t = C_0 \times e^{-k_1 t} \tag{9}$$

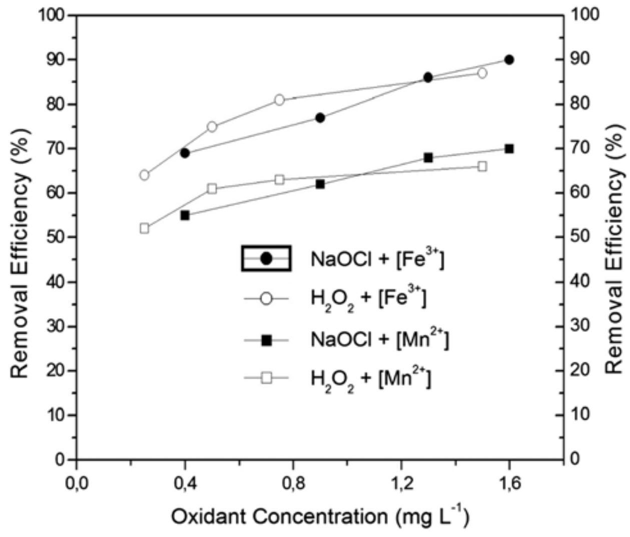

Fig. 2. Sulphide removal efficiency by catalytic oxidation with NaOCl and H_2O_2 ([Fe^{3+}] = 1.2 mg L^{-1}, [Mn^{2+}] = 1.0 mg L^{-1}; [S^{2-}]$_{initial}$ = 148 mg L^{-1}; pH = 6.6; $T = 293$ K).

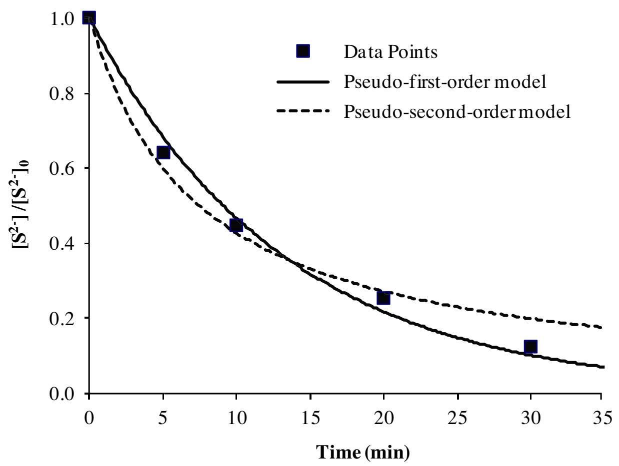

Fig. 3. Kinetics of sulphide concentration with contact time: data points and kinetic models (air + [Fe^{3+}] = 1.2 mg L^{-1}; [S^{2-}]$_{initial}$ = 161 mg L^{-1}; pH = 6.6; $T = 293$ K).

$$C_t = \frac{C_0}{1 + k_2 C_0 t} \tag{10}$$

where C_0 is the initial sulphide concentration and C_t is the concentration of sulphide ($\mathrm{mol\,L^{-1}}$) at time t, k_1 and k_2 are the pseudo-first- and pseudo-second-order rate constants in $\mathrm{s^{-1}}$ and $\mathrm{L\,mol^{-1}\,s^{-1}}$. The values of rate constants in case of the two models at various temperatures are provided in Table 2. Model goodness was evaluated through the calculation of RSD and R^2. The performances of two models were compared by using the F-test [36,37]. F_{cal} is defined as

$$F_{\mathrm{cal}} = \frac{S_R^2(\mathrm{A})}{S_R^2(\mathrm{B})} \tag{11}$$

where S_R^2 (A) and S_R^2 (B) are, respectively, the model variances of models A and B. F_α and α are, respectively, the critical value tabulated and the level of confidence. In general, the residual variance of the model expected to produce the better fitting is placed in the denominator (model B). If $F_{\mathrm{cal}} > F$, the model corresponding to the denominator is statistically better than the other, according to the chosen level of significance ($\alpha = 0.05$). Results for a 95% confidence level show that the difference is not statistically significant.

One of the first studies on the mechanism of catalytic oxidation of H_2S was conducted on activated carbon and the overall reaction rate of oxidation of H_2S was found to be first order in H_2S, which is in accordance with our modeling results [38]. In our case, the pseudo-first-order model seems to fit better, to experimental data as seen in Fig. 3, although the difference between the two models was not statistically significant. Also, under the conditions of continuous air supply into the liquid phase, the oxygen coverage of the catalyst surface was assumed to be constant during the oxidation process. Under these conditions, the reaction rate becomes independent of the oxygen concentration [39].

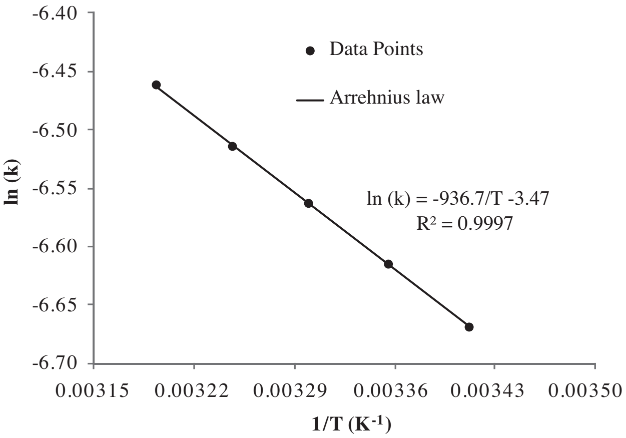

Fig. 4. Temperature dependency of the catalytic oxidation of sulphide according to the Arrhenius equation (air + $[\mathrm{Fe^{3+}}]$ = $1.2\,\mathrm{mg\,L^{-1}}$; $[\mathrm{S^{2-}}]_{\mathrm{initial}} = 161\,\mathrm{mg\,L^{-1}}$; pH = 6.6); T = 293, 298, 303, 313 K).

3.3.2. Activation energy

The influence of the temperature on the kinetic rate can be expressed mathematically by the Arrhenius equation:

$$\ln k = \ln k_0 - \frac{E_a}{R}\frac{1}{T} \tag{12}$$

where R is the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}K^{-1}}$), T is the temperature (K), E_a is the activation energy ($\mathrm{J\,mol^{-1}}$), k_0 is a temperature-independent factor and k is the kinetic constant ($\mathrm{s^{-1}}$, from the pseudo-first kinetic model). An Arrhenius plot using the k values is shown in Fig. 4. The activation energy for the sulphide catalytic oxidation can be obtained from the slope of the linear plot of ln k against $1/T$. The values of k_0 and E_a were reported to be 0.031 ± $0.002\,\mathrm{s^{-1}}$ and 7,788 ± $84\,\mathrm{J\,mol^{-1}}$, respectively. The value of E_a obtained in the present study is in close agreement with those obtained by other researchers [38–40]. The difference in some values could be due to the types and nature of catalysts in various studies [41].

Table 2
Estimated pseudo-first-order and second-order kinetic model parameters (value ± relative standard deviation)

T (K)	Pseudo-first-order model			Pseudo-second-order model			Test F	
	$k_1 \times 10^3$ ($\mathrm{s^{-1}}$)	R^2	$S_R^2 \times 10^8$ ($\mathrm{mol\,L^{-1}})^2$	k_2 ($\mathrm{L\,mol^{-1}\,s^{-1}}$)	R^2	$S_R^2 \times 10^8$ ($\mathrm{mol\,L^{-1}})^2$	F_{cal}	$F_{1-\alpha}$
293	1.27 ± 0.07	0.994	2.53	0.45 ± 0.05	0.987	5.16	2.0	
298	1.34 ± 0.07	0.994	2.71	0.47 ± 0.05	0.988	5.06	1.9	
303	1.41 ± 0.09	0.993	3.25	0.51 ± 0.05	0.988	4.89	1.5	6.4
308	1.5 ± 0.1	0.991	4.30	0.54 ± 0.06	0.989	4.51	1.1	
313	1.6 ± 0.1	0.989	5.05	0.58 ± 0.06	0.990	54.27	1.2	

4. Conclusions

In the present study, abatement of sulphide from the refinery wastewater was studied by the catalytic oxidation process. The results exhibited that Fe^{3+} acts as an effective catalyst in the presence of oxygen. The maximum removal efficiency of 90% was achieved using an Fe^{3+} concentration of $2.4\,mg\,L^{-1}$ in the presence of oxygen. The kinetics of the process was completed in *ca*. 30 min. It was observed that with the increase in temperature from 298 to 313 K, the sulphide removal efficiency increased slightly. Pseudo-first-order model fitted well to the experimental data. NaOCl + $[Fe^{3+}]$ combination was found to be the most effective for sulphide removal and a concentration of $1.6\,mg\,L^{-1}$ NaOCl yielded the maximum sulphide removal efficiency (*ca*. 93%). The achieved sulphide removal obtained in this study was found relatively higher than the efficiency obtained in the oxidation tanks in the WWTP, *Galp Energia*. Thus, the results of the present study suggest that Fe^{3+} + oxygen or NaOCl + $[Fe^{3+}]$ can be economically and effectively used for the treatment of sulphide containing wastewater.

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References

[1] A. Coelho, A.V. Castro, M. Dezotti, J.G.L. Sant'Anna, Treatment of petroleum refinery sourwater by advanced oxidation processes, J. Hazard. Mater. 137 (2006) 178–184.

[2] X. Zhao, Y. Wang, Z. Ye, A.G.L. Borthwick, J. Ni, Oil field wastewater treatment in biological aerated filter by immobilized microorganisms, Process Biochem. 41 (2006) 1475–1483.

[3] S. Marshall, Pollutant Removal Handbook, Noyes Data Corporation, Park Ridge, NJ, 1973.

[4] E. Vaiopoulou, P. Melidis, A. Aivasidis, Sulfide removal in wastewater from petrochemical industries by autotrophic denitrification, Water Res. 39 (2005) 4101–4109.

[5] W. Andrew, Environmental Consequences of and Control Processes for Energy Technologies, Noyes Data Corporation, Argonne National Laboratory, New Jersey, 1990.

[6] A.G. Rao, K.K. Prasad, G.V. Naidu, N.C. Rao, P.N. Sarma, Removal of sulfide in integrated anaerobic–aerobic wastewater treatment system, Clean Technol. Environ. 6 (2003) 66–71.

[7] S. Jacobs, S. Reiber, M. Edwards, Sulfide induced copper corrosion, J. Am. Water Works Assoc. 90 (1998) 62–73.

[8] J.P. Gudas, H.P. Hack, Parametric evaluation of susceptibility of Cu-Ni alloys to sulfide induced corrosion in sea water, Corrosion 35 (1979) 259–264.

[9] T.L. Lyn, J.S. Taylor, Assessing sulfur turbidity formation following chlorination of hydrogen sulfide in ground water, J. Am. Water Works Assoc. 84 (1992) 103–112.

[10] M. Tomar, T.H.A. Abdullah, Evaluation of chemicals to control the generation of malodorous hydrogen-sulfide in wastewater, Water Res. 28 (1994) 2545–2552.

[11] A. Kotronarou, M.R. Hoffmann, Catalytic autooxidation of hydrogen sulfide in wastewater, Environ. Sci. Technol. 25 (1991) 1153–1160.

[12] F.J. Millero, S. Hubinger, M. Fernandez, S. Garnett, Oxidation of H_2S in seawater as a function of temperature, pH, and ionic strength, Environ. Sci. Technol. 21 (1987) 439–443.

[13] R.E. Train, Quality Criteria for Water, Castle House, London, 1979.

[14] J.E. Palumbo, L.C. Brown, S.C. Stratton, Modeling the oxidation of sulfide in pulp and paper wastewaters, J. Environ. Eng. 136 (2010) 1171–1179.

[15] NSF, Behavior of H2S in the atmosphere and its effects on vegetation, Report to the National Science Foundation, in, National Science Foundation, Washington, DC, 1976.

[16] J.M. Hill, The acute toxicity of hydrogen sulphide-a literature review and application to storm sewage discharges, Water Research Centre, Medmenham, 1984.

[17] T. Hvitved-Jacobsen, Sewer Processes: Microbial and Chemical Process Enginneering of Sewer Networks, CRC Press, Boca Raton, FL, 2002.

[18] A.H. Nielsen, P. Lens, J. Vollertsen, T. Huitved-Jacobsen, Sulfide-iron interactions in domestic wastewater from a gravity sewer, Water Res. 39 (2005) 2747–2755.

[19] P.K. Dutta, R.A. Rozendal, Z. Yuan, K. Rabaey, J. Keller, Electrochemical regeneration of sulfur loaded electrodes, Electrochem. Commun. 11 (2009) 1437–1440.

[20] P.K. Dutta, K. Rabaey, Z. Yuan, R.A. Rozendal, J. Keller, Electrochemical sulfide removal and recovery from paper mill anaerobic treatment effluent, Water Res. 44 (2010) 2563–2571.

[21] I. Pikaar, R.A. Rozendal, Z. Yuan, J. Keller, K. Rabaey, Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities, Water Res. 45 (2011) 2281–2289.

[22] J. García De Lomas, A. Corzo, J.M. Gonzalez, J.A. Andrades, E. Iglesias, M.J. Montero, Nitrate promotes biological oxidation of sulfide in wastewaters: Experiment at plant-scale, Biotechnol. Bioeng. 93 (2006) 801–811.

[23] L. Zhang, P. De Schryver, B. De Gusseme, W. De Muynck, N. Boon, W. Verstraete, Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review, Water Res. 42 (2008) 1–12.

[24] T. Sakai, K. Sawada, N. Ohi, A kinetic study of liquid phase oxidation of sodium sulfide with oxygen catalyzed by sulfur black B dye, J. Chem. Eng. Japan 13 (1980) 331–334.

[25] Y. Ueno, A. Williams, F.E. Murry, A new method for sodium sulfide removal from an aqueous solution and application to industrial wastewater and sludge, Water, Air, Soil Pollut. 11 (1979) 23–42.

[26] A.H. Nielsen, T. Huitved-Jacobsen, J. Vollertsen, Effect of iron on chemical sulfide oxidation in wastewater from sewer networks, J. Environ. Eng. 133 (2007) 655–658.

[27] N. Takenaka, S. Furuya, K. Satoshi, H. Bandow, Y. Maeda, Y. Furukawa, Rapid reaction of sulfide with hydrogen peroxide and formation of different final products by freezing compared to those in solution, Int. J. Chem. Kinet. 35 (2003) 198–205.

[28] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), American Water Works Association (AWWA) & Water Environment Federation (WEF), Washington, DC, 2005.

[29] Association Française de Normalisation (AFNOR), Huile essentielle de Néroli, T75-202, Paris, 1976.

[30] N.A. Padival, W.A. Kimbell, J.A. Redner, Use of iron salts to control dissolved sulfide in trunk sewers, J. Environ. Eng. 121 (1995) 824–829.

[31] D.A. Dohnalek, J.A.F. Patrick, The chemistry of reduced sulfur species and their removal from ground water supplies, J. Am. Water Works Assoc. 75 (1983) 298–308.

[32] J. Herszage, M.A. dos Santos Afonso, The autooxidation of hydrogen sulfide in the presence of hematite, Colloids Surf. Physicochem. Eng. Aspects 168 (2000) 61–69.

[33] V.K. Sharma, J.O. Smith, F.J. Millero, Ferrate(VI) oxidation of hydrogen sulfide, Environ. Sci. Technol. 31 (1997) 2486–2491.

[34] F. Cadena, R.W.J. Peters, Evaluation of chemical oxidizers for hydrogen sulfide control, J Water Poll. Cont. Fed. 60 (1988) 1259–1263.

[35] N. Ahmad, S. Maitra, B.K. Dutta, F. Ahmad, Remediation of sulfidic wastewater by catalytic oxidation with hydrogen peroxide, J. Environ. Sci. 21 (2009) 1735–1740.

[36] D.C. Montgomery, G.C. Runger, Applied Statistic Probability for Engineers, Wiley, New York, NY, 1999.

[37] D.C. Montgomery, Design Analysis of Experiments, Wiley, New York, NY, 2001.

[38] R. Sreeramamurthy, P.G. Menon, Oxidation of H_2S on active carbon catalyst, J. Catal. 37 (1975) 287–296.

[39] St. Christoskova, M. Stoyanova, M. Georgieva, Low temperature catalytic oxidation of sulfide ions in aqueous solutions on a Ni-oxide system, React. Kinet. Catal. Lett. 70 (2000) 139–145.

[40] A.K. Dalai, A. Majumdar, A. Chowdhury, E.L. Tollefson, The effects of pressure and temperature on the catalytic oxidation of hydrogen sulfide innatural gas and regeneration of the catalysts to recover the sulfur produced, Can. J. Chem. Eng. 71 (1993) 75–82.

[41] A.K. Dalai, A. Majumdar, E.L. Tollefson, Low temperature catalytic oxidation of hydrogen sulfide in sour produced wastewater using activated carbon catalysts, Environ. Sci. Technol. 33 (1999) 2241–2246.