

Vol. 29, No. 3, 2023, 152-162 e-ISSN: 2721-4885 DOI: https://doi.org/10.36706/jtk.v29i1.1509 Online at http://ejournal.ft.unsri.ac.id/index.php/jtk

Remidiation of sodium hydrogen sulphide rayon waste by oxidation method

I. Wulansari^{1,*}, Wahyudi B. Sediawan², M. Hidayat²

¹Chemical Polymer Engineering, Politeknik STMI Jakarta, Jakarta, Indonesia ²Chemical Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia *Correspondence: ismawulansari@kemenperin.go.id

Abstract

The mechanism of the oxidation reaction at various concentrations of sulfide waste is dominated by the direct reaction between sulfide waste and hydrogen peroxide to reduce NaHS compounds. Sodium hydrogen sulfide is easily oxidized with oxygen in the air so that a substance will form which triggers air and water pollution through an increase in the value of chemical oxygen demand. This study aims to determine the effect of adding an oxidizing agent on the rate of reduction of sulfide compounds, the effect of pH, temperature, reaction time between the oxidizing agent and sulfide waste, the amount of oxidizing agent and total sulfur concentration and to model experimental data mathematically. In this study, the kinetic equations and activation energies of H₂O₂ and NaHS were determined based on the total sulfur and sulfate in oxidation reaction solutions. The percentage of sulfide removal is influenced by the initial sulfide waste concentration and the NaHS/H₂O₂ ratio. The NaHS/H₂O₂ ratio of 1:17.5 gave the best sulfide removal percentage of 89.95 % with an initial sulfide waste concentration of 6,136 mg/L. Oxidation reactions did not show a different percentage of sulfide reduction, which was in the range of 76 - 85 %. The optimum NaHS/H₂O₂ ratio composition can determine optimal conditions for air pollution control, corrosion levels and waste treatment costs as a result of the formation of spent sulfidic caustic compounds consisting of sulfur ions, sulfate ions. Oxidation of sulfides to sulfates by H₂O₂ can be applied to sulfide waste containing SH- ions.

Keywords: hydrogen peroxide, oxidation, potassium permanganate titration, rayon waste, sodium hydrosulphide

How to Cite: Wulansari, I., Wahyudi, B., Fitriyana, Hidayat, M. (2023). Remidiation of sodium hydrogen sulphide rayon waste by oxidation method. Jurnal Teknik Kimia, 29(3), 152-162. https://doi.org/10.36706/jtk.v29i3.1509

1. INTRODUCTION

The rayon industry generates a considerable amount of chemical waste that contains a mixture of inorganic and organic elements. The rayon segment's clean technology transition initiative aims to minimize waste while rendering trash a supplementary resource in industrial development. As a result of the reaction between H₂S and NaOH during the scrubbing process, NaHS with a COD concentration of 476.72 kg/m³ is produced. Compounds that emit scents are the source of rayon factory waste. A thorough examination of all odor sources is performed. To identify all emission sources, all emission sources that can't be prevented throughout chemical

operations are recorded, characterized, and evaluated. The majority of air pollution in the rayon manufacturing industry is caused by pollutants created through the scrubbing phase before the material reaches the subsequent processing systems (Po, 2014).

Sulfide compounds effluent is created by rayon plants. There are essentially two methods to eliminate sulfide waste: the dry method, that involves photocatalytic oxidation, which plasma removal, ozonation, and adsorption, and the wet method, which involves complex absorption, biological methods, alkali absorption, ionic liquid absorption, catalytic oxidation, and chemical oxidation (Y. Wang et al., 2018). The most prevalent approach for removing sulfide from chemically produced waste and waste water is a sulfate-forming reaction. The chemical oxidation technique converts SH^- ions to sulfate (SO_4^{2-}) (Afonso, 2012) and using hydrogen peroxide as an oxidizer (Jabari, 2012). A greater concentration ratio of HS^- and H_2O_2 is required to produce sulfate as the primary product.

A significant concentration proportion can shorten the reaction time and increase the total amount of sulfates requiring four times the amount of H_2O_2 to be produced (Vaiopoulou et al., 2016). The significant advantage of hydrogen peroxide over other potential oxidizing agents is that the degradation of H_2O_2 produces just oxygen and water. Although the hydrogen peroxide compound is liquid, hence is capable of being administered swiftly and readily, it is not hazardous or caustic, and it is economically comparable with other oxidation substances used in industrial systems (Mamat et al., 2020). The addition of a substance that oxidizes to a liquid containing impurities for an oxidation process where the oxidizing agent is immediately introduced to the solution is a traditional chemical processing procedure. Some of the most common chemical oxides are chlorine, chlorine dioxide, oxygen, persulfate, permanganate, ozone, and hydrogen peroxide. Another use of chemical oxidation is waste treatment and water quality improvement.

Table 1. The oxidation reaction products studied and several previous studies in reducing sulfide components

Product	Acidity	Condition	Ratio	Ref
S_x^{-2} , SO_3^{2-} , S^0 , $S_2O_3^{2-}$, SO_4^{2-}	6 – 12	Control	0,06 – 1,25	(Fan et al., 2011)
S^0 , S^{2-} , $S_2O_3^{2-}$, SO_4^{2-}	8	Control	0,25 - 2,5	(Xu et al., 2013)
S ⁰ ,S ₂ O ₃ ²⁻ , SO ₃ ²⁻ , SO ₄ ²⁻	>12	Control	1 - 2	(Ntagia et al., 2019)
SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , SO ₄ ²⁻	4 - 5	Uncontrol	0,3 - 2	(Alipour & Azari, 2020)

The reaction of hydrogen peroxide with hydrogen sulfide is influenced by various parameters such as pH, temperature and initial concentration of hydrogen peroxide. These variables have a significant impact on the product and reaction time. Substitution of hydrogen peroxide into the process can increase COD reduction efficiency. However, the concentration of hydrogen peroxide must be controlled if the amount of hydrogen peroxide in the system is too high, then the hydrogen peroxide will react with hydroxyl radicals and produce the weak radical H₂O. Sulfide oxidation occurs when sulfides react with hydrogen ions. The ratio of reactant coefficients affects

the desired product and the mole ratio of certain reactants such as reactions 1 - 3 as follows (Alipour & Azari, 2020).

$$OH^*_{(g)} + H_2O_{2(l)} \rightarrow H_2O_{(l)} + HO_2^*_{(g)}$$
 (1)

$$HS_{(1)}^{-} + 4 H_2O_{2(1)} \rightarrow SO_4^{-2}(1) + 4 H_2O_{(1)} + H_{(q)}^{+}$$
 (2)

$$H^{+}_{(g)} + HS^{-}_{(l)} + H_{2}O_{2(l)} \rightarrow S^{o}_{(aq)} + 2 H_{2}O_{(l)}$$
 (3)

Through a comparable reactant concentration ratio, which is also the reaction between HS^- and H_2O_2 causes the pH to rise, and the pH value generally decreases once bisulfate is formed. The overall quantity of sulfur in the form of sulfate will be smaller in a reaction regarding four times higher H_2O_2 concentrations (Alipour & Azari, 2020). The implications of adding oxidizers via the oxidation technique on the reduction rate of sulfide compounds is investigated in this research. The objective of this study is to determine the efficacy of sulfide removal is in rayon waste with varying oxidant concentrations. When analyzing the operational aspects of chemical oxidation, mathematical modeling of experimental data is utilized to determine the kinetics of the events that occur. This configuration is used on rayon waste from the chemical sector to examine the success of sulfide remediation in the rayon industry.

2. MATERIALS AND METHODS

To eliminate odors and sulfides, sulfide waste undergoes processing in phases. The initial concentration of sulfide and hydrogen peroxide is determined in the first step. The second stage involves calculating the quantity of sulfide in the active solution, which is known as the NaHS/H $_2$ O $_2$ ratio. An oxidation process between sulfide and H $_2$ O $_2$ occurs in the third step. In this part, the concentrations of NaHS and H $_2$ O $_2$ are reduced so that the sulfide and peroxide content emitted from the batch reactor at set operating conditions is the reaction's residual sulfide and peroxide. Sulfide waste is obtained from the H $_2$ S scrubbing process from gas streams in the rayon industry using NaOH solution. The chemicals for the oxidation process are H $_2$ O $_2$ from PT Peroxide Indonesia Pratama, as well as Fe $_3$ SO $_4$.7H $_2$ O $_5$ O $_4$ 98%, Na $_2$ C $_2$ O $_4$ 99% and KMnO $_4$ 99% from Merck. The dimensions of the glass stirrer submerged in the working solution with a height of 11.5 cm are 2.5 cm from the bottom of a 1 L three-neck flask with the stirring speed maintained at 300 - 350 rpm (Wulansari, 2023).

Determination of concentration and standardization of potassium permanganate with a 0.25N Potassium Permanganate solution was standardized by adding a 0.1 N Na $_2$ C $_2$ O $_4$ solution to a 1 M H $_2$ SO $_4$ solution. The KMnO $_4$ standardization procedure was carried out by adding a 0.1 N Na $_2$ C $_2$ O $_4$ solution and heating it to 90 – 95 °C for thirty minutes. Titrate with KMnO $_4$ solution until the Na $_2$ C $_2$ O $_4$ solution changes color to pink. The concentration of H $_2$ O $_2$ was determined through a titration process using a 0.25 N KMnO $_4$ solution. The method to determine the initial concentration of hydrogen peroxide is to dilute the H $_2$ O $_2$ solution in 1 M H $_2$ SO $_4$ solution. The 10 ml H $_2$ O $_2$ solution is titrated with the KMnO $_4$ solution until the color changes to pink.

Determination of the initial concentration and physical properties of sulfide waste by diluting 20 ml of concentrated sulfide waste into 100 ml of distilled water. Determination of the initial concentration of sodium hydrosulfide by dissolving NaHS in 1 M H₂SO₄ solution. The NaHS solution is titrated with KMnO₄ solution until the color changes to pink (Santos Junior et al., 2020). Oxidation reaction and sulfide analysis

method with a 233 ml of sulfide waste was put into a vessel and H_2O_2 solution was added. The color of the sulfide waste will change from dark yellow to clear. The solution that produces oxidation is mixed with sodium solids from side reactions formed through the filtration process. To carry out the analysis, the KMnO4 solution was used after the filtrate was dissolved in a 1 M H_2SO_4 solution. The samples were then analyzed at different time intervals for 60 minutes. The oxidation resulting compound is heated to a temperature of 70 - 80 $^{\circ}$ C using an electric stove (Ahmad et al., 2014).

3. RESULTS AND DISCUSSION

The aim of this research is to analyze the total residual sulfide concentration using an oxidation process under non-isothermic operating conditions. The parameters observed in this study were total sulfide concentration, sulfate concentration, pH and temperature. These parameters will be measured for each variation of the research process, namely the NaHS/H₂O₂ ratio, operating temperature and initial concentration of sulfide waste. The heat of reaction that occurred obtained a value of Δ Hr for the oxidation reaction of sulfide waste of -1,285.23 kJ/mol. The enthalpy value shows a negative value so that the reaction that occurs is exothermic. The calculated Δ G° value is -1,223.43 kJ/mol and the K value is 2.44 x 10²¹⁴. A negative Δ G° value indicates that the reaction is irreversible. Based on the results of observations of the Δ G° value, the chemical equilibrium constant at a temperature of 25 °C has a very large K value, this shows that the oxidation reaction of sulfide waste runs in the same direction without any reverse reaction. A negative enthalpy value causes the sulfide oxidation reaction to experience a drastic increase in temperature in the first minute and then decrease as the reaction time progresses.

3.1. EFFECT OF SULFIDE CONCENTRATION ON OXIDATION REACTIONS

Sulfide waste processing generally consists of several methods such as adding chemical compounds in the form of oxidizers or precipitators. Through chemical processing methods including oxidation, precipitation and neutralization, where the neutralization process is carried out by adding acid in the form of H_2O_2 to the spent caustic solution which is alkaline. The oxidation method with hydrogen peroxide is the oxidation method with the most widespread application. Free radicals contained in hydrogen peroxide have oxidation potential which has an effect on increasing the percentage of sulfide removal in waste (N. Wang et al., 2016).

The sulfite concentration changes very little in the reaction during the 24 hour reaction period so it is assumed that the sulfite compound has reached a steady state concentration, namely when the rate of sulfite formation from sulfide oxidation is the same as the rate at which sulfite is oxidized to sulfate (Mamat et al., 2020). With this assumption, the sulfite oxidation rate constant (k₃) can be determined from experimental and kinetic data in Reaction (4):

$$k_2 C_{SO_3^{-2}} C_{O_2} = k C_{SH^{-p_1}} C_{H_2 O_2}^{p_2}$$
 (4)

The oxidation reaction proposed in this research is an overall formation reaction where the reaction does not always show the combination of molecules that actually occurs. There were three experiments on the distribution of reactants and products that were carried out, namely the distribution of concentrations of reduced bisulfide, sulfur, sulfite and thiosulfate and which were the result of side reactions categorized

as total measured sulfide against reaction time. Based on Figure 1, the sulfide concentration shows a constant decreasing curve with every increase in the initial sulfide concentration of 6,136 mg/L which experiences a lower slope as the ratio increases. It can be seen from this difference that the reaction with a NaHS/H₂O₂ ratio of 1:5.6 produces the most optimum difference in reducing the sulfide concentration. The solids formed during the oxidation process consist of sulfur, Na₂SO₄, Na₂SO₃, Na₂S₂O₃ and Na₂S₃O₆. The rate of solids formation and total solids mass are influenced by reaction time, concentration of initial waste sulfide solution and operating temperature.

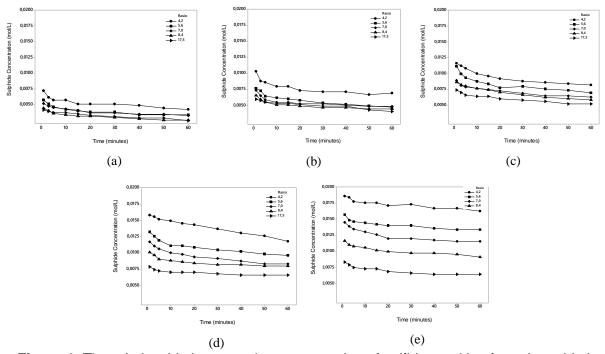


Figure 1. The relationship between the concentration of sulfide resulting from the oxidation reaction and the reaction time at various initial concentrations (a) 902 mg/L, (b) 1,742 mg/L, (c) 2,434 mg/L, (d) 3,693 mg/L and (e) 6,136 mg/L at various NaHS/ H_2O_2 ratios

3.2. EFFECT OF SULPHATE CONCENTRATION

Chemical oxidation of sulfides is believed to be a chain oxidation reaction so that the reaction is very sensitive to reaction conditions. There is some correlation between the length of the induction period and the initial oxidation rate in that the length of the induction period decreases with increasing initial oxidation rate (Vaiopoulou et al., 2016). At low pH, sulfide essentially forms as hydrogen sulfide which reacts with hydrogen peroxide and forms elemental sulfur. Under high pH conditions, sulfide will form as H_2S therefore, hydrogen peroxide is best used at low pH levels. At high pH levels four times more hydrogen peroxide is needed so that the S_2 ion can be converted into sulfate. Based on Figure 2, it is known that the relationship between total sulfate and reaction time at various initial concentrations and the ratio shows that as the reaction time increases and the amount of H_2O_2 in the solution increases, more and more sulfate is formed. From Figure 2, it can be seen that increasing the concentration of hydrogen peroxide does not provide a fluctuating increase in sulfate formation.

The stoichiometry of chemical sulfide oxidation is very complex because various products and intermediates will be produced during the reaction process. The

main intermediate products identified are elemental sulfur (S_0), thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}) while sulfate (SO_4^{2-}) is a reaction product. The formation of intermediate products and formed products is described in reactions (Alipour & Azari, 2020):

$$2HS_{(l)}^{-} + O_{2(l)} \rightarrow 2S_{(s)}^{0} + 2OH_{(l)}^{-}$$
(5)

$$2HS_{(l)}^{-} + 2O_{2(l)} \rightarrow S_2O_3^{2-}(s) + H_2O_{(l)}$$
(6)

$$2HS_{(I)}^{-} + 3O_{2(I)} \rightarrow 2SO_{3}^{2-}(s) + 2H_{(I)}^{+}$$
(7)

$$2HS_{(I)}^{-} + 4O_{2(I)} \rightarrow 2SO_{4}^{2-}(s) + 2H_{(I)}^{+}$$
(8)

The reaction with excess H₂O₂ conditions will result in a sulfide oxidation reaction which has a tendency to form sulfate. The concentration of sulfate formed has a relatively constant value so that the addition of hydrogen peroxide in an amount that is very far from the stoichiometric ratio does not provide optimum results, such as at an initial sulfide concentration of 1,742 mg/L, a sulfate concentration of 0.0217 -0.0238 mol/L is obtained. Reactions containing sulfur content with unknown component compounds will definitely assume that all the sulfide contained will be oxidized to sulfate (Takenaka et al., 2003). By adding excessive amounts of hydrogen peroxide, the pH of the solution can be changed. Thus, it is hoped that the concentration and composition of samples carried out in isothermal or non-isothermal conditions can be changed by changing the temperature and concentration of hydrogen peroxide in the reaction solution. The addition of an amount of H₂O₂ exceeding the stoichiometry is carried out to reduce the problem of odor or corrosion in the solution and to shorten the reaction time to around fifteen minutes where in waste that will undergo oxidation a minimum time of fifteen minutes will be required for the reaction to complete.

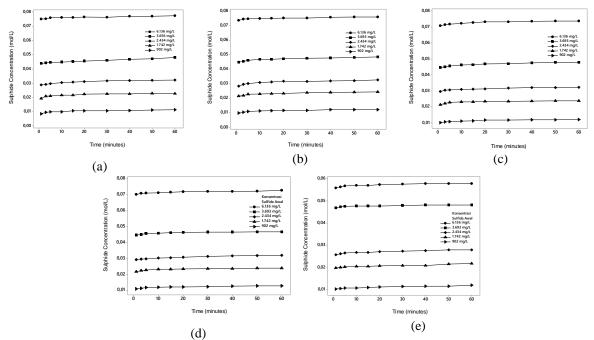


Figure 2. The relationship between total sulfate resulting from the oxidation reaction and reaction time at various NaHS/ H_2O_2 ratios (a) 1 : 4.2; (b) 1 : 5.6; (c) 1 : 7; (d) 1 : 8.4 and (e) 1 : 17.5

3.3. EFFECT OF SULFIDE REMOVAL EFFICIENCY ON OXIDATION REACTION RATE

Table 2. Reaction order profiles and reaction rate constants from fitting results as well as reaction removal efficiency at various $NaHS/H_2O_2$ ratios

902	±	0,5	mg	/L
-----	---	-----	----	----

Ratio	T (°C) pł		H		n, no	l _k	Removal		SSE	
NaHS/H ₂ O ₂	1'	60'	1'	60'	· p ₁	p ₂	κ -	1'	60'	JOL
4.2	33	31	6.98 ± 0.06	7.22 ± 0.06				0.54	0.73	0.08
5.6	33	31	6.93 ± 0.06	6.67 ± 0.06	2.99 1.3		1.38 148,517 -	0.63	0.78	0.08
7.0	33	30	6.89 ± 0.05	6.44 ± 0.06		99 1.38		0.66	0.79	0.09
8.4	33	30	6.83 ± 0.05	5.90 ± 0.05				0.71	0.83	0.07
17.5	34	30	6.16 ± 0.05	4.21 ± 0.05				0.71	0.83	0.16

$1,742 \pm 1 \text{ mg/L}$

Datia NaUC/U O	T (°C)		pH					Removal		
Ratio NaHS/H ₂ O ₂	1'	60'	1'	1' 60' p ₁ p ₂ K	K	1'	60'	SSE		
4.2	39	33	7.26 ± 0.06	7.52 ± 0.06	_			0.65	0.77	0.05
5.6	37	33	7.11 ± 0.06	6.80 ± 0.06	2.99 1.51		0.74	0.84	0.05	
7.0	36	33	6.81 ± 0.05	6.60 ± 0.05		1.51	1 73,181	0.74	0.83	0.06
8.4	37	32	6.77 ± 0.05	6.40 ± 0.05				0.77	0.84	0.06
17.5	35	32	6.80 ± 0.06	4.17 ± 0.05	_			0.77	0.84	0.17

2,434 ± 1 mg/L

Ratio NaHS/H ₂ O ₂	T (°C)		р	рН		n	le	Ren	SSE	
Natio Nano/n2O2	1'	60'	1'	60'	- p ₁	p_2	N.	1'	60'	SSE
4.2	37	33	7.43 ± 0.06	8.45 ± 0.06	_ _ 2.99		1.59 42,337	0.71	0.80	0.05
5.6	38	33	7.13 ± 0.06	6.71 ± 0.06				0.72	0.82	0.06
7.0	38	32	6.67 ± 0.05	6.50 ± 0.06		1.59		0.77	0.84	0.07
8.4	39	33	6.54 ± 0.05	6.35 ± 0.05				0.77	0.85	0.09
17.5	38	32	5.68 ± 0.05	3.94 ± 0.05				0.78	0.84	0.16

$3,693 \pm 0.5 \text{ mg/L}$

Ratio NaHS/H ₂ O ₂	T (°C)		рН		n.		l.	Removal		SSE
	1'	60'	1'	60'	p ₁	p ₂	K	1'	60'	SSE
4.2	46	33	7.82 ± 0.06	8.61 ± 0.06				0.74	0.80	0.05
5.6	45	33	6.76 ± 0.06	6.32 ± 0.06				0.77	0.83	0.06
7.0	43	32	6.24 ± 0.06	5.75 ± 0.05	2.99 1.77	1.77 20,054	0.79	0.85	0.06	
8.4	43	33	6.05 ± 0.05	5.44 ± 0.05			0.81	0.85	0.07	
17.5	40	32	4.97 ± 0.05	3.62 ± 0.05	_			0.83	0.86	0.11

$6,136 \pm 1 \text{ mg/L}$

		pН		n.		le.	Rem	SSE	
1'	60'	1'	60'	ρ1	p_2	K	1'	60'	SSE
59	37	8.33 ± 0.06	9.00 ± 0.06				0.80	0.83	0.03
57	37	6.78 ± 0.06	6.28 ± 0.06				0.82	0.85	0.06
56	37	6.20 ± 0.06	5.85 ± 0.06	-	.11 17,888	0.83	0.86	0.07	
55	36	6.08 ± 0.06	5.78 ± 0.06			-	0.86	0.89	0.06
51	36	5.14 ± 0.06	4.00 ± 0.06				0.87	0.90	0.06
	1' 59 57 56	1' 60' 59 37 57 37 56 37 55 36	1' $60'$ $1'$ 59 37 8.33 ± 0.06 57 37 6.78 ± 0.06 56 37 6.20 ± 0.06 55 36 6.08 ± 0.06	1' $60'$ 1' $60'$ 59 37 8.33 ± 0.06 9.00 ± 0.06 57 37 6.78 ± 0.06 6.28 ± 0.06 56 37 6.20 ± 0.06 5.85 ± 0.06 55 36 6.08 ± 0.06 5.78 ± 0.06	1' 60' 1' 60' 91' 59 37 8.33 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 57 37 6.78 ± 0.06 6.28 ± 0.06 9.00 ± 0.06 56 37 6.20 ± 0.06 5.85 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 55 36 6.08 ± 0.06 5.78 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06	1' 60' 1' 60' p1 p2 59 37 8.33 ± 0.06 9.00 ± 0.06 8.33 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.06 9.00 ± 0.		$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	

Sulfide removal efficiency in this study is defined as the reaction conversion that takes place between sulfide waste and hydrogen peroxide where removal efficiency is the reduction of the initial amount of sulfide in the reaction to the final amount of sulfide during the reaction. The results of testing the effect of initial sulfide concentration on the percentage of sulfide removal show that the % removal obtained after 10 minutes of the sulfide removal process is the best time to reduce sulfide in various initial waste concentrations and reaction ratios. The peak point of the curve has an interest in shifting towards the 10 minute. The shift in the optimum point of sulfide removal for a concentration of 3,605 mg/L was 74.67 %, 79.45 %, 81.12 %, 83.49 % and 84.37 %.

The decreasing rate of increase in removal percentage is indicated by the formation of a % removal curve with time that is increasingly approaching zero slope so that increasing reaction time does not significantly affect the sulfide removal percentage. A curve with zero slope, apart from being influenced by the reaction time, is also influenced by the addition of the NaHS/ H_2O_2 ratio, where increasing the ratio can increase the % removal point at the start of the reaction so that the reaction produces a straight line approaching zero slope. Increasing the ratio can increase the amount of H_2O in the solution. As a result, the initial concentration of sulfide contained will be less than with a minimum addition ratio, and will be closer to the stoichiometric mole. The percentage of sulfide removal increased along with the initial sulfide concentration value. This is due to the fact that the interaction of hydroxyl radicals is reduced when they bond with each other in the liquid phase. The hydroxyl radicals formed are more likely to undergo direct reactions with sulfides rather than recombining the hydroxyls to produce hydrogen peroxide, as shown in the following reaction (Alipour & Azari, 2020).

$$OH^*_{(g)} + OH^*_{(g)} \to H_2O_{2(l)}$$
 (9)

Based on this explanation, a small NaH_8/H_2O_2 ratio will optimize sulfide removal, this is because the reaction rate constant of sulfide with hydrogen peroxide is greater than the known recombination reaction rate constant of 5 x 10^9 M/s (Syaichurrozi et al., 2020). Based on Table 2, the oxidation reaction order states the sum of all the exponents of conversion and concentration as well as the influence of the involvement of NaHS and H_2O_2 reactant concentrations on the oxidation reaction rate equation. The kinetic equation is applied in programming to determine the value of k, where k is defined as the oxidation reaction rate constant which is specific for the reaction with the initial sulfide concentration and the NaHS/ H_2O_2 ratio.

Calculation of reaction kinetics to determine the reaction rate constant and reaction order was carried out using the Isqnonlin fitting method in MATLAB. Linear data regression is carried out to determine the gradient that occurs along a linear curve by determining data points so that it is ensured that the data with curve fitting will form a linear regression deviation. Determining the sum of squared error was carried out to determine the deviation of each data with the fitting results for each component in this study. Error calculations were carried out for the values of sulfide concentration, H₂O₂ concentration and % removal which was marked by the reaction conversion value. Reducing the initial concentration of sulfide increases the SSE value. This is due to the addition of H₂O to the sulfide waste which causes the solution concentration to decrease so that the sensitivity of the analysis becomes greater and causes the measurement and fitting data to show a greater SSE value.

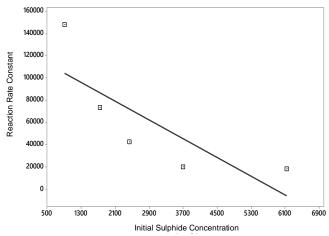


Figure 3. Reaction rate constant profile against initial sulfide concentration

In the case of increasing the NaHS/ H_2O_2 ratio, the difference in higher SSE values is not considered significant, so the conclusion from the fitting results is that increasing the oxidation ratio is able to increase the final conversion in the time span from the first to the 60 minute, with the final conversion ranging between 0.73 - 0.89. Reactions with a p_2 order close to zero do not depend on the overall H_2O_2 concentration, so H_2O_2 does not make a significant contribution to increasing the reaction rate. The relationship between the reaction rate constant and the initial sulfide concentration at various $NaHS/H_2O_2$ ratios, where increasing the reaction concentration tends to decrease the reaction rate constant, is as shown in Figure 3. This relationship shows that for each ratio, the reaction rate constant will decrease. An initial sulfide concentration of less than 2,500 mg/L causes a significant decrease in reaction rate.

4. CONCLUSION

The generation of hydroxyl radicals, which will react with ions, will increase the productivity of the SH⁻ oxidization procedure as the quantity of hydrogen peroxide gets higher. Sulfide waste can be converted into sulfates which reduces COD levels and makes the waste safe for disposed of in the surrounding environment. To produce the optimal sulfide waste management product, the NaHS/H₂O₂ proportion must be chosen. The beginning waste concentration of 3,605 mg/L is the best waste sulfide concentration elimination value, that is determined by the percentage of sulfide reduction and the increase in temperature during the oxidation process. The initial concentration of sulfide waste at a constant NaHS/H₂O₂ ratio will rise as the proportion of sulfide removed rises. The quantity of hydrogen peroxide in the solution grows in proportion to the amount of solids formed during oxidizing. The optimal pH range is between 5.4 and 7.8. Standardization is required on a regular basis to assess the quantities of waste sulfide and hydrogen peroxide, which reduced with the duration of product shelf life

ACKNOWLEDGEMENT

The author would like to thank Chemical Polymer Engineering Politeknik STMI Jakarta Ministry of Industry of the Republic of Indonesia and the Chemical Engineering Postgraduate Program at Gadjah Mada University for the research support and PT Rayon Utama Makmur Sukoharjo, Central Java which has provided sodium hydrosulfide as sulfide waste for this research.

REFERENCES

- Afonso, J. F. P. e J. C. (2012). New Strategies For Treatment and reuse of Spent Sulfidic Caustic Stream From Petroleum Industri. *Quimica*, *35*(7), 1449.
- Ahmad, N., Ahmad, F., & Khan, I. (2014). Studies on the Oxidative Removal of Sodium Thiosulfate from Aqueous Studies on the Oxidative Removal of Sodium Thiosulfate. October. https://doi.org/10.1007/s13369-014-1473-0
- Alipour, Z., & Azari, A. (2020). COD removal from industrial spent caustic wastewater: A review. *Journal of Environmental Chemical Engineering*, 8(3), 103678. https://doi.org/10.1016/j.jece.2020.103678
- Fan, X., Hao, H., Shen, X., Chen, F., & Zhang, J. (2011). Removal and Degradation Pathway Study of Sulfasalazine with Fenton-like Reaction. *Journal of Hazardous Materials*, 190(1–3), 493–500. https://doi.org/10.1016/j.jhazmat.2011.03.069
- Jabari, M. Al. (2012). Spent Caustic Treatment Using Advanced Oxidation Processes (Issue May).
- Mamat, M. C., Bustary, A. B., & Azoddein, A. A. M. (2020). Oxidation of sulfide removal from petroleum refinery wastewater by using hydrogen peroxide. *IOP Conference Series: Materials Science and Engineering*, 736(2). https://doi.org/10.1088/1757-899X/736/2/022103
- Ntagia, E., Fiset, E., da Silva Lima, L., Pikaar, I., Zhang, X., Jeremiasse, A. W., Prévoteau, A., & Rabaey, K. (2019). Anode materials for sulfide oxidation in alkaline wastewater: An activity and stability performance comparison. *Water Research*, *149*, 111–119. https://doi.org/10.1016/j.watres.2018.11.004
- Po, W. (2014). Treatment of Hydrogen Sulfide. *International Publication Number*, 2(12), 1–25.
- Santos Junior, J. J. P., Pereira, R. G., Rosendahl, M., Santo Filho, D. M. E., & Gouveia, J. M. G. (2020). The use of ethanol to determine the volume of a pycnometer used to measure the density of liquids at different temperatures and pressures. *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, *42*(1). https://doi.org/10.1007/s40430-019-2107-y
- Syaichurrozi, I., Sarto, S., Sediawan, W. B., & Hidayat, M. (2020). Mechanistic models of electrocoagulation kinetics of pollutant removal in vinasse waste: Effect of voltage. *Journal of Water Process Engineering*, *36*(October 2019), 101312. https://doi.org/10.1016/j.jwpe.2020.101312
- Takenaka, N., Furuya, S., Sato, K., Bandow, H., Maeda, Y., & Furukawa, Y. (2003). Rapid Reaction of Sulfide with Hydrogen Peroxide and Formation of Different Final Products by Freezing Compared to Those in Solution. *International Journal* of Chemical Kinetics, 35(5), 198–205. https://doi.org/10.1002/kin.10118

- Vaiopoulou, E., Provijn, T., Prévoteau, A., Pikaar, I., & Rabaey, K. (2016). Electrochemical sulfide removal and caustic recovery from spent caustic streams. *Water Research*, *92*, 38–43. https://doi.org/10.1016/j.watres.2016.01.039
- Wang, N., Zheng, T., Zhang, G., & Wang, P. (2016). A Review on Fenton-Like Processes for Organic Wastewater Treatment. *Environmental Chemical Engineering*, *4*(1), 762–787. https://doi.org/10.1016/j.jece.2015.12.016
- Wang, Y., Wang, Z., & Liu, Y. (2018). Oxidation Absorption of Gaseous H2S Using Fenton-Like Advanced Oxidation Systems [Research-article]. *Energy and Fuels*, 32(11), 11289–11295. https://doi.org/10.1021/acs.energyfuels.8b02657
- Wulansari, I. (2023). Sulfide Removal By Catalitic Oxidation From Rayon Waste. Journal of Research and Community Service, 4(2), 615–623.
- Xu, X., Chen, C., Lee, D. J., Wang, A., Guo, W., Zhou, X., Guo, H., Yuan, Y., Ren, N., & Chang, J. S. (2013). Sulfate-reduction, sulfide-oxidation and elemental sulfur bioreduction process: Modeling and experimental validation. *Bioresource Technology*, 147, 202–211. https://doi.org/10.1016/j.biortech.2013.07.113