The Oxidation of Sulphide Compounds in the Order of Processing Sodium Hydrosulphides

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Abstract - *Oxidation of spent sulfidic caustic consist of SH- ion or NaHS compound by H_2O_2 in neutral or acidic solution to elemental sulphur may provide a convenient and economical method for the control of sulphide wastes and their associated odors at pulp, paper and textile industry. The effects of total sulphide concentration, isothermal and nonisothermal process, catalyst loading, ratio of SH^-/H_2O_2 and temperature on the kinetics of sulphide oxidation were investigated. Kinetic equations and activation energies of H_2O_2 and SH- ion to total sulphur and sulphate in aqueous solution for the non catalytic and catalytic oxidation reaction were calculated based on the experimental results. The rate of SSC oxidation was found higher at lower initial sulphide concentration and the rate of sulphide oxidation was found directly proportional to loading and hydrogen peroxide addition. Optimum total sulphide concentration was achieved when sulphide solutions were treated at pH 4 in the presence of H_2O_2 in the ratios SH^-/H_2O_2 1:5.6. The potential user of H_2O_2 determine the optimal conditions for control of odor, corrosion and waste treatment cost due to SSC consisting of sulphur ion, sulphate ion, etc. The oxidation of sulphides into sulphates by H_2O_2 may be applied directly to aqueous wastes containing these odorants.*

1. Introduction

Rayon is composed of regenerated cellulose although manufactured fibres in which substituents below 15% of the hydrogens at the hydroxyl groups by the Federal Trade Commission [1]. The industrialization process also encourages the rayon industry to produce chemical waste containing a mixture of inorganic and organic components in large quantities which is burdening the environment. Waste reduction is driving the chemical industry towards clean technology as a secondary resource. Waste processing in the rayon industry is carried out appropriately to generate secondary waste resources while the mixing of several compounds in the waste stream provenience from liquid-liquid contact between NaOH and H_2S. Immediately, sodium hydroxide the majority react with H_2S becomes sodium hydrosulphide or sodium waste as spent sulfidic caustic (SSC) [2,3].

Sodium sulphide (Na_2S) and sodium hydrosulphide (NaHS) are reaction products of the scrubbing H_2S with NaOH solution by the Eq. (1), (2), [4] and (3)[5]. Sodium hydrosulphide can occur as predominant sulphide species in waste, therefore the reaction product is influenced by the pH

of the spent NaOH solution is required. Once, the pH of Eq 1 is generate at pH > 12, when the pH ease around 11.5, NaSH is formed [5, 6]. The following equations describe the scrubbing reaction of H_2S and NaOH solution:

$$H_2S + 2\ NaOH \rightarrow Na_2S + 2\ H_2O \tag{1}$$
$$H_2S + NaOH \rightarrow NaSH + H_2O \tag{2}$$
$$H_2S + Na_2S \rightarrow 2\ NaSH \tag{3}$$
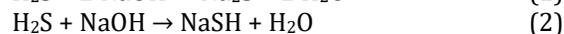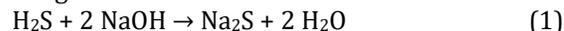
Sulphur compounds as SH- ion at spent sulfidic caustic can be removed through wet air oxidation, fenton's oxidation with precipitation using a mixture of ferrous and ferric salts, chemical oxidation with catalytic or non catalytic with hydrogen peroxide, oxidation of H_2S and Na_2S in aqueous solution by dissolved oxygen, incineration with auxiliary fuel, and biological oxidation of sulphide. However, these methods of treatment are expensive, using a mixture of ferrous and ferric salts is competitive process, and induce secondary pollution problems [3], [7]–[14].

For the reduce of sulphide from waste and wastewater the most prevalent process involves its oxidation to a more benign form sulphate [15]–[25]. In the chemical oxidation method, ions SH- are converted into sulphate (SO_4^{2-}) species [7], with the oxidants are hydrogen peroxide, sodium

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hypochlorite, potassium permanganate, chlorine and ferrate (VI) ions [26]. The oxidation of sulphide using hydrogen peroxide at low temperatures that the decomposition of sulphide was five times faster at 258 K than at room temperature [27].

The noncatalytic oxidation method is carried out the reaction occur sulphide waste and H_2O_2 without the addition of a catalyst, where the sulphide can be completely removed from a solution through a chemical oxidation process. Hydrogen peroxide will react with sulphides below pH 7 to form sulphur and above 8 to form sulphate according to the reaction below [7, 25, 26]:

$$HS^- + H_2O_2 \rightarrow H_2O + OH^- + S \qquad (4)$$
$$HS^- + 4 H_2O_2 \rightarrow 4 H_2O + SO_4^{2-} + H^+ \qquad (5)$$
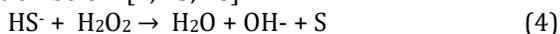
The sulphide concentration may not be estimated in a redox system between oxidants (H_2O_2) and reductants (S^{2-}) own time. The total sulphide be necessary analyzed to determine concentration of sulphate and reduction of sulphide in sulphide waste. The analysis was carried out by reacting the sulphide waste after being oxidized, with a solution of potassium permanganate as the reaction below [30]:

$$5 NaHS + 8 KMnO_4 + 7 H_2SO_4 \rightarrow 4 K_2SO_4 + 8 MnSO_4 + 7 H_2O + 5 NaOH \qquad (6)$$
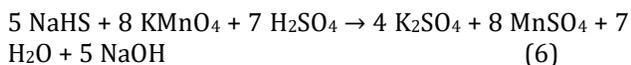
The initial concentration of H_2O_2 was determined by titration method using potassium permanganate solution [28, 29]. The H_2O_2 titration method using potassium permanganate solution with the following reaction equation [31]:

$$5 H_2O_2 + 2 KMnO_4 + 3 H_2SO_4 \rightarrow K_2SO_4 + 2 MnSO_4 + 8 H_2O + 5 O_2 \qquad (7)$$
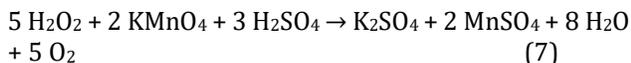
The objective of this study is to investigate the effect of two experimental variables viz. the initial sulphide waste concentration and ratio $NaHS/H_2O_2$, which may affect the total sulphide concentration and considerable sulphide to sulphate during hydrogen peroxide oxidation of NaHS onto subsequent synthesis of NaSH. The effect of time, pH, temperature, total solid, and density were examined in order to use as indicators for specify of the reaction end point during industrial operation. Besides, the hydrogen peroxide and initial sulphide waste concentration was analyzed by potassium permanganate titration to examine the initial condition and the optimum oxidation condition.

2. Material and Methodology
2.1. Materials and Reagent
The sulphide waste used in this study was collected from PT Rayon Utama Makmur, a synthetic textile and rayon industry located in Sukoharjo, Indonesia. It had a pH value of 11.75 (base), contained COD of 476.72 kg/m3. Another material used was hydrogen peroxide, sulphuric acid, distilled water, potassium permanganate and sodium oxalate, all of the material was provided by Merck. Hydrogen peroxide with the concentration of 30% wt was obtained from PT Peroksida Indonesia Pratama. It had a pH value of 3.9 (acidic), contained initial concentration of 2.44 M. Sulphuric acid with the concentration of 96% wt used for

nalysis, it had a initial concentration of 1 M. Sodium oxalate had a normality of 0.1 N used as a primary standard for standardization $KMnO_4$ solution. Potassium permanganate had concentration from standardization of 0.05 M.

2.2 Experimental Set Up
Sodium hydrosulphide was put in a three neck flask and stirred by a glass agitator with volume of 500 L, it was used as batch reactor. Subsequently, the obtained quantities of total sulphide was, first, added into sodium hydrosulphide, then followed by hydrogen peroxide as slowly. Volume of sodium hydrosulphide treated in this study was 199 – 351 mL depending ratio of $NaHS/H_2O_2$. The dimension of the glass agitator immersed in working solution was 2.5 cm from the bottom of three neck flask, it speed was defended to be 300 - 350 rpm.

2.3 Experimental Design and Procedure
Three neck flask support was used when the reaction under non-isothermal conditions with temperature to be 30 – 57oC. The temperature of working solution was measured using a mercury thermometer (range 0 – 100°C) while acidity was measured by digital pH meter Kedida model CT-6022. The temperture and pH following the start of each reaction was recorded every 1, 3, 5, 10, 15, 20, 30, 40, 50, and 60 min. Five different moles of hydrogen peroxide were tested with ratio of $NaHS/H_2O_2$ is 4.2 ; 5.6 ; 7 ; 8.4 ; and 17.5 moles H_2O_2/moles NaHS. Furthermore, a working solution was withdrawn for analysis, 12 mL of the sample solution was filtered using filter paper by Whatman 40 and allowed to separate from solid. The filtered liquid was analysis with potassium permanganate titration of APHA Standard Method for the Examination of Water and Wastewater 20th ed 3500-Mn to calculated total sulphide, standardization potassium permanganate and hydrogen peroxide, while solid on working solution was dried at temperature range of 110 – 130°C until 3 hours after which it was weighted. The filter paper was dried for 30 minutes after which it was weighted to dried weight. In other words, the decrease in volume was assumed due to evaporation and reduction processes of working solution for analysis. Left pigure shows the experimental set up in this study.

2.4. Materials Standardization and Initial Condition
The chemicals for standardization and initial condition of waste used included potassium permanganate ($KMnO_4$) 0.25 N, sulphuric acid, sodium oxalate and distilled water. The potassium permanganate 0.25 N was prepared by dissolving 7.9 g $KMnO_4$ in distilled water and making up to 1 L. It was heated for 1 or several hours near the boiling point, then filter and standardize with sodium oxalate. The sodium oxalate 0.1 N was prepare by dissolving 0.67 gr of $Na_2C_2O_4$ in 100 mL concentrated H_2SO_4 1 M and stir to dissolve. The sulphuric acid 1M was prepared by dilute 27.8 mL H_2SO_4 95.8% in distilled water with making up to 500 mL and allowed to cool at room temperature.
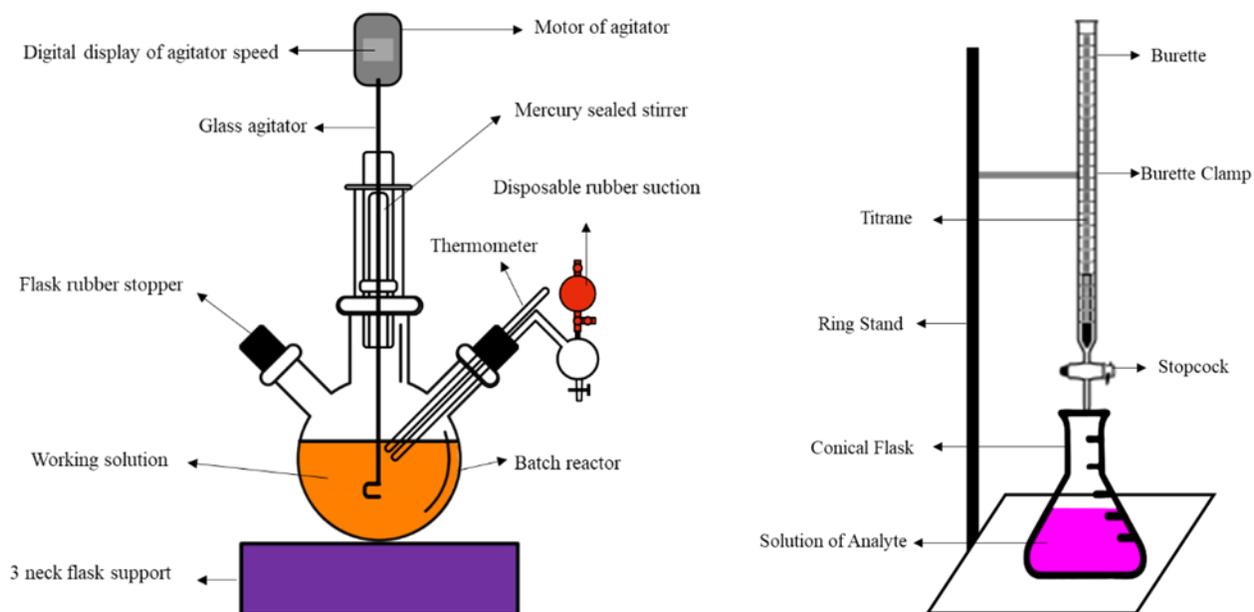
Figure 1. Experimental set up (a) isothermal and nonisothermal process, (b) titration and standardization

The procedure of standardization potassium permanganate was put 5 mL of $Na_2C_2O_4$ solution into a 250-mL erlenmeyer flask and heat rapidly to 90 to 95°C (do not let temperature < 85°C). Titrate rapidly with the $KMnO_4$ solution to be standardized, while stirring, to a slight pink end-point color

The hydrogen peroxide standardization procedure was as follows: (1) 10 ml of hydrogen peroxide 50% was dilute in 100 mL concentrated H_2SO_4 1 M into a 250-mL volumetric flask, (2) 10 ml of hydrogen peroxide solution was put into a 250-mL erlenmeyer flask, (3) heat the solution to fall below 70°C on a hot plate, (4) futhermore, put down the flask from heater and titrate the solution with $KMnO_4$ from a 50-mL burette until the first appearance to a slight pink end-point color that persists for 30 seconds. Futhermore, the normality of hydrogen peroxide from standardization was calculated by using Eq. (9).

$$Normality\ of\ KMnO_4 = \frac{g\ Na_2C_2O_4}{mL\ KMnO_4 \times 1,40\ 01} \quad (8)$$

$$Normality\ of\ H_2O_2 = Normality\ of\ KMnO_4 \times mL\ KMnO_4 \quad (9)$$

The sodium hydrosulphide initial concentration was as follows: (1) 10 ml NaHS solution was put into a 250-mL erlenmeyer flask, (2) 10 mL sulphuric acid were added to it, (3) heat the solution to fall below 70°C on a hot plate, (4) put down the flask from heater and titrate the solution with $KMnO_4$ from a 50-mL burette until a slight pink end-point color that persists for 30 seconds. Futhermore, the initial concentration of sodium hydrosulphide (C_{NaHS0}) was calculated by using Eq. (10).

$$C_{NaHS\ 0} = \frac{N_{KMnO_4} \times mL\ KMnO_4}{80} \quad (10)$$

2.5. Total Sulphide Analysis

The procedure of total sulphide analysis was put 4 mL of working solution and 16 mL H_2SO_4 1 M into a 100-mL erlenmeyer flask and heat rapidly below 90°C. Titrate

that persists for at least 1 min. If necessary, warm beaker contents during titration, in addition, pottasium permanganate has to be standardized daily against with $Na_2C_2O_4$ solution [33]. Hence, calculation normality of potassium permanganate expressed in Eq. (8).

rapidly with the $KMnO_4$ solution to analyzed, while stirring, to a slight pink end-point color that persists for at least 1 min. Hence, concentration of total sulphide (C_{NaHS}) subsequent to oxidation was expressed in Eq. (11).

$$C_{NaHS} = \frac{(N_{KMnO_4} \times mL\ KMnO_4) - 0.4 \times (i-4) \times n_0}{3.20\ 01 \times mL\ sample} \quad (11)$$

3. Results and Discussion
3.1. Physical Properties of Initial Sulphide Waste

There are some advantages to sulphide precipitation is considerable used in industry, enclose the lower solubility of metal sulphide precipitates, probability to metal removal preference, to measure off reaction rates, rectify settling properties and capability for reuse of sulphide precipitates [34]. However, sulphide precipitation is visible elaborate to control particularly regarding the toxicity and corrosiveness of excess sulphide [34, 35]. Sulphide precipitation might conducted using either sulphide coumpound such as FeS and CaS, sulphide aqueous solution viz. Na_2S, NaHS NH_4S, $Na_2S_2O_3$, and gaseous sulphide sources to wit H_2S. The thermodynamic equilibria involved in metal sulphide precipitation can be expressed as [34] :

$$H_2S \overset{Kp1}{\longleftrightarrow} HS^- + H^+ \ ; \ Kp1 = \frac{[HS^-][H^+]}{[H_2S]} \ ; pK_1 = 6.99 \quad (12)$$

$$HS^- \overset{Kp2}{\longleftrightarrow} S^{2-} + H^+ \ ; \ ; \ Kp2 = \frac{[S^{2-}][H^+]}{[HS^-]} \ ; \ pK_2 = 17.4 \quad (13)$$
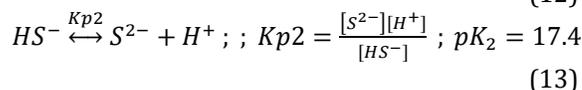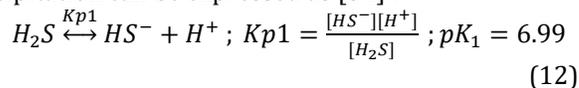
The concentration of sulphur constiturent is a strong function of pH [34], as shown in Fig 3 shows the relationship between temperature, pH and density, then pH and density

will abatement with intensify temperature of sulphide waste. During the heating process until 100°C, an orange precipitate and inflict crystalline structure is materialize in sulphide waste solution which is thought to be sulphur. So as the temperature sulphide waste intensify rise, it will be settle and degrade density of solution.
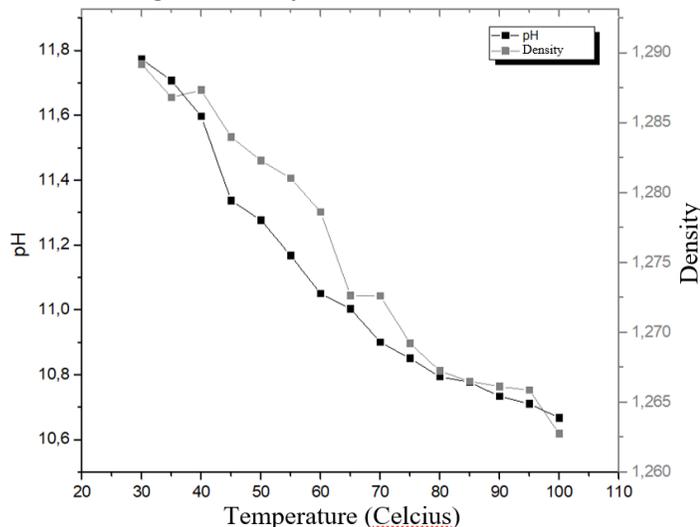

Figure 2. The relationship between temperature, pH and density raw sulphide waste

3.2. pH and Temperature Profile

The oxidation reaction is a pH and temperature suspended process in that pH appear an important role in the decomposition of sulphide to sulphate generation in the oxidation reaction at Eq. 4 and 5. The effect of the initial and oxidation pH value of sulphide waste on the total sulphide removal by the oxidation reaction was studied in the pH range of 7 to 11 for initial pH to adjust the pH value reaction and 3.5 to 9 by adding H_2O_2 as proceeds oxidation process. The experiment was conducted to investigate the affect of pH and temperature on the degradation sulphide concentration process efficiency and find the trend of temperature and optimum pH oxidation. The results obtained are presented in Figure 3 showing the profile of time and pH during oxidation of sulphide at kind initial sulphide concentration, and Figure 4 showing that time and temperature at initial sulphide concentration 6,136 ; 3,605 ; 2,434 ; 1,742 ; and 902 mg[SH^-]/L. As shown in Figure 3, the experiment at 3,605 mg[SH^-]/L have pH 3.5 to 7 with initial pH 9 has the best stable pH value for each ratio NaHS/ H_2O_2. As the amount of H_2O_2 in the oxidation reaction increase, the oxidation efficiency was also increase. As shown in Figure 4, the at 3,605 mg[SH^-]/L have best trend temprature degradation

from 46 to 36°C, which runways reaction has been controlled.

3.3. Percentage Solid Profile

The solid during oxidation was forecast by using Eq. (4) and (5) then shown in Figure 5 that profile percentage solid between time during oxidation of sulphide at initial sulphide concent   6,136; 3,605; 2,434; 1,742 ; and 902 mg[SH^-]/L. Furthermore, Figure 5 showed the how much (%) the solid was separated by filteration on experimental procedure. Commonly, the % solid generate during oxidation reaction was decreased through reaction time except 1,742 and 902 mg[SH^-]/L and turbidity working solution was pale during oxidation for all variation of initial sulphide concentration and ratio NaHS/ H_2O_2. The % solid at 10 – 15 minutes were higher sodium solid formed, that are sulphur, Na_2SO_4, $Na_2S_2O_3$, $Na_2S_3O_6$, etc.

3.4. Total Sulphide Concentration Profile

The oxidation product rate of intermediate sulfite oxidation to sulfate depend on being of hydrogen peroxide and pH, there is rapidly oxidation rate in an oxidizing environment, may be simplified as [15]:

$$S^{2-} \rightarrow S_2O_3^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-} \tag{14}$$
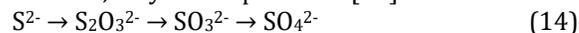
The pH of sulphide waste solution is highly alkaline, it can be close pH 6 - 7 by adding acid solution such H_2SO_4 or HCl but H_2S could be generated in the solution, so to ignore the formation of H_2S that could escape from the solution to some extent. However the oxidation proceeds may reduction sulfide concentration and the pH also [15]. The Figure 6 represent profil sulfide concentration with time oxidation reaction for five different initial sulphide consentration at variety of moles hydrogen peroxide. The same amount of hydrogen peroxide 4.2, 5.6, 7, 8.4, and 17.5 times mole of sulphide waste was enhanced to batch reactor of 500 mL sulphide waste solution. The initial rate of sulfide oxidation showed an majority dependence on the initial sulphide concentration. The whole of sulphide concentration arrise higher at a considerable of initial suphide concentration and ratio NaHS/H_2O_2. Beginning with 6,136 mg[SH^-]/L of initial sulfide solution, complete 82-87% removal of the sulfide was achieved within about 1 to 5 min, but that concentration is high risk to industrial process applied in that runaway reaction uncontrol. Figure 6 shows the effect of initial concentration loading which was varied from 6,136 to 902 mg[SH^-]/L in 500 mL feed solution. The time of 90% sulfide removal varies deficient than 10 min. The rate and temperature increases rapidly with restricted of ratio NaHS/H_2O_2, it is 4.2 moles.
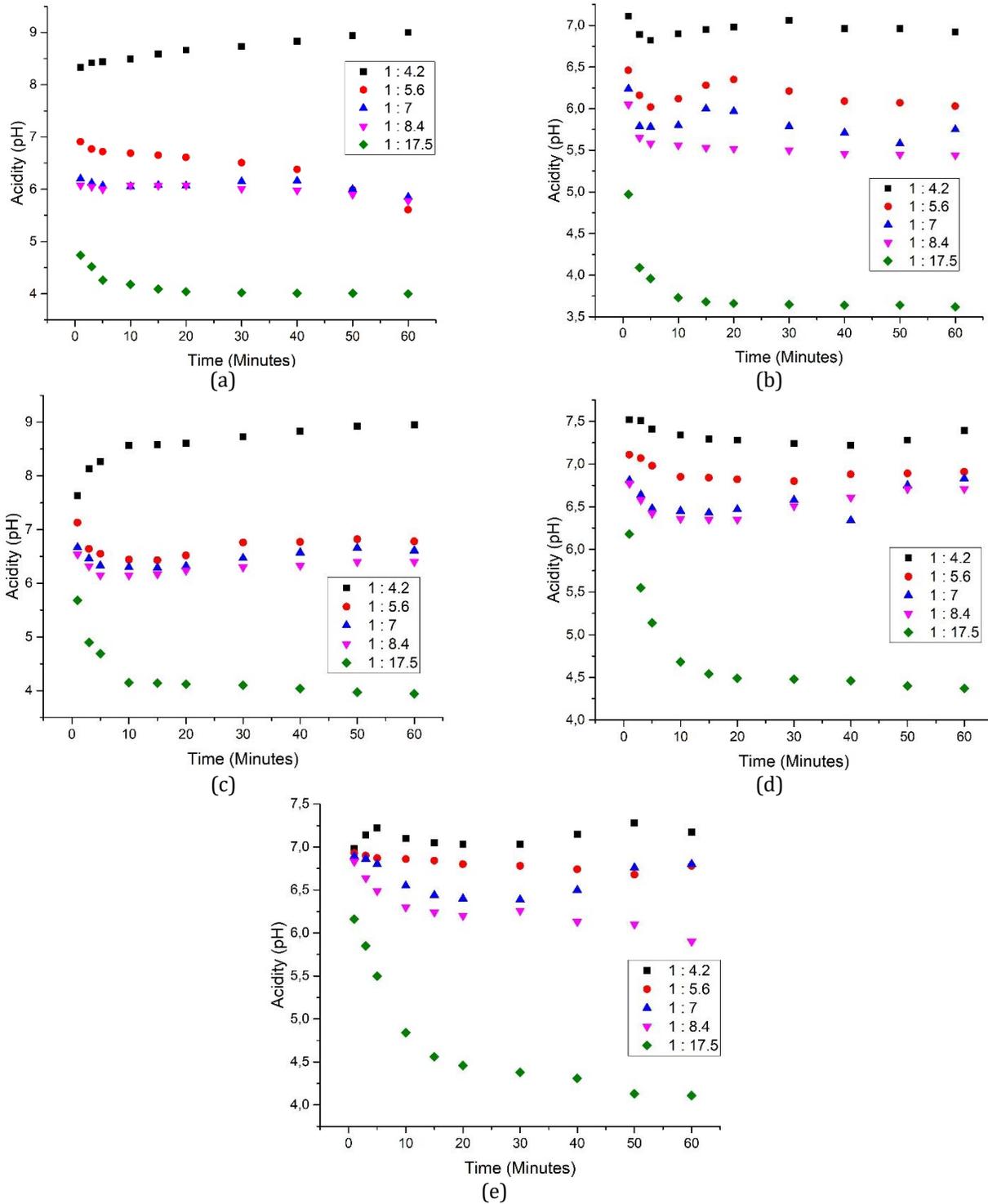
Figure 3. Relationship between time and pH during oxidation of sulphide at sulphide concentration (a) 6,136; (b) 3,605; (c) 2,434; (d) 1,742; and (e) 902 mg[SH⁻]/L
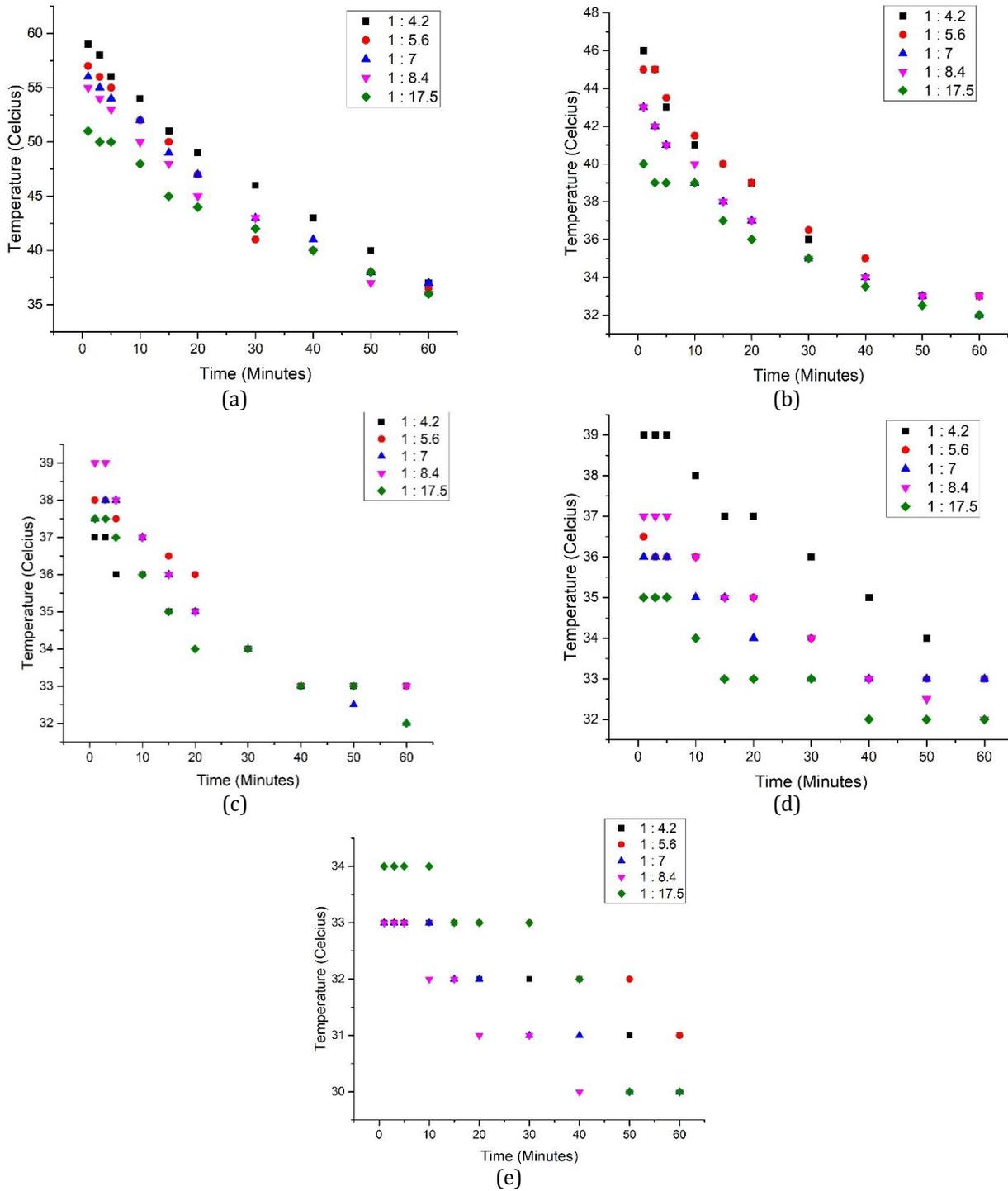
Figure 4. Relationship between time and temperature during oxidation of sulphide at sulphide concentration (a) 6,136; (b) 3,605; (c) 2,434; (d) 1,742; and (e) 902 mg[SH$^-$]/L

(a)

(b)

(c)

(d)

(e)
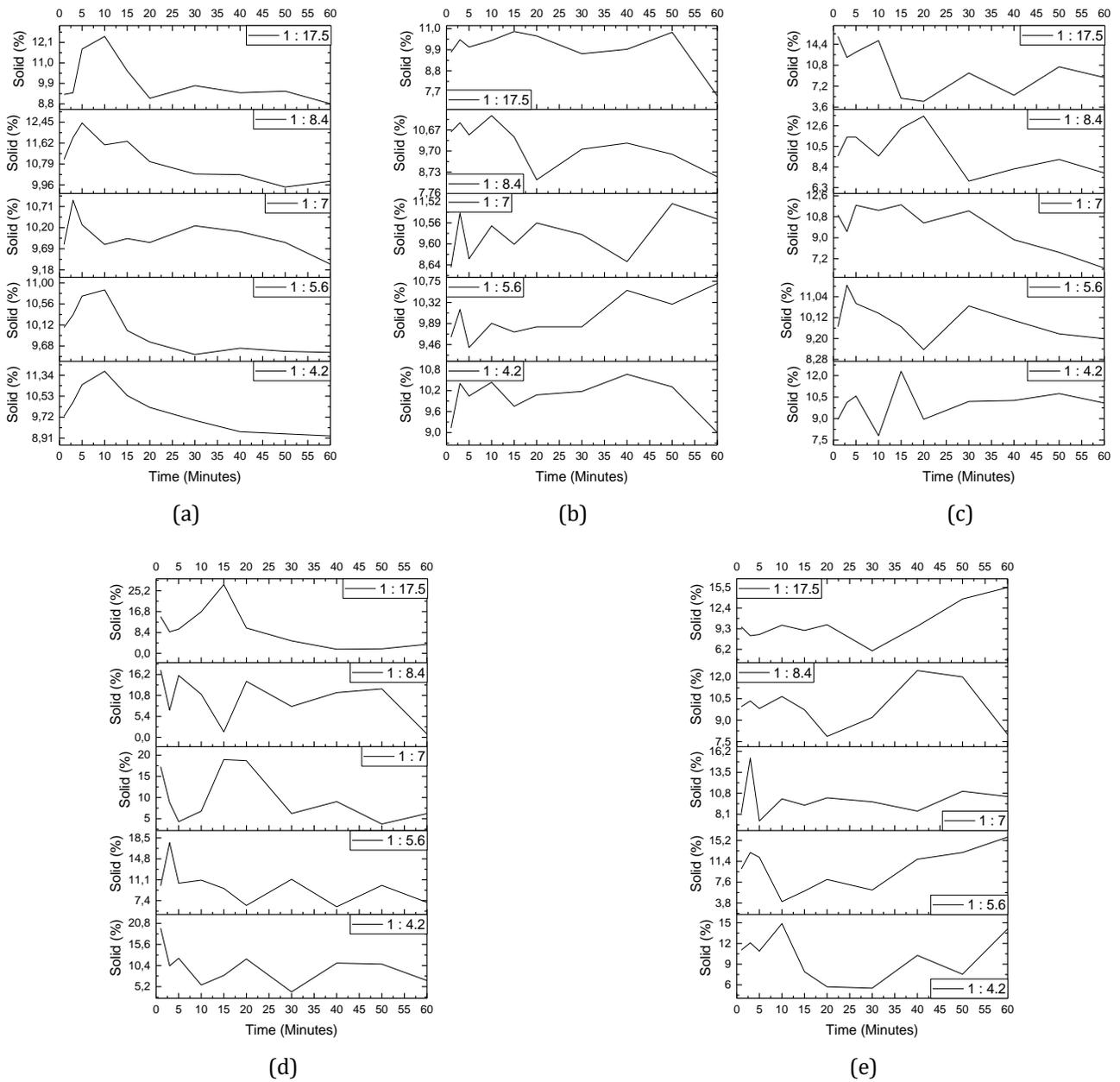
Figure 5. Percentage solid between time during oxidation of sulphide at sulphide concentration (a) 6,136; (b) 3,605; (c) 2,434; (d) 1,742; and (e) 902 mg[SH⁻]/L
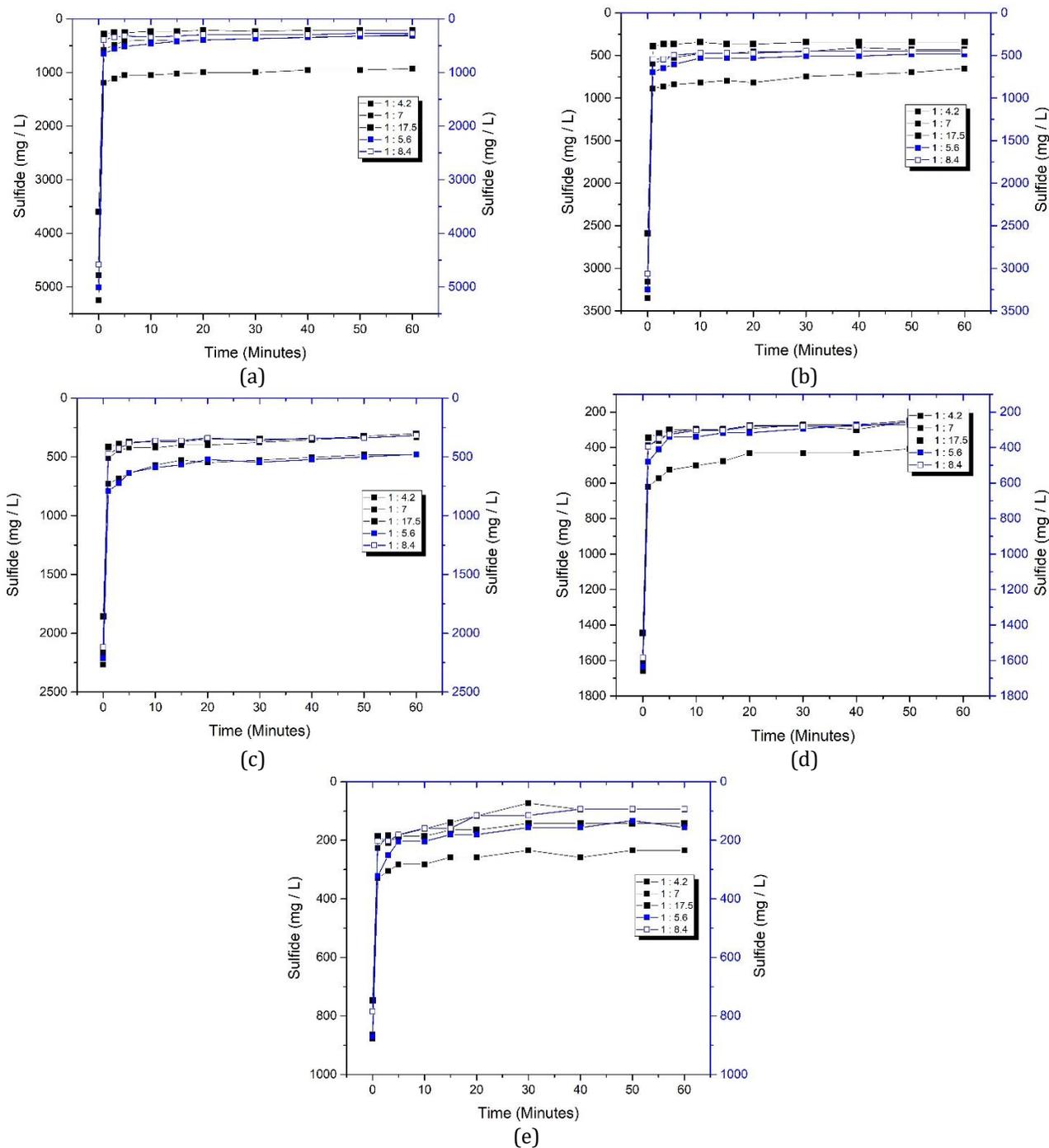
Figure 6. Profil time and total sulphide concentration during oxidation of sulphide at initial sulphide concentration (a) 6,136 ; (b) 3,605 ; (c) 2,434 ; (d) 1,742 ; and (e) 902 mg[SH⁻]/L

4. Conclusion

The sulphide concentration removal in an aqueous solution was accomplished by chemical oxidation process. From the present work following conclusions can be drawn: (1) rate of sulfide oxidation was found higher at considerable of initial suphide concentration and ratio NaHS/H_2O_2 initial sulfide concentration; (2) rate of sulfide

oxidation was immediately compatible to non catalyst loading reaction and moles ratio of hydrogen peroxide addition; (3) at uncontrol temperature rate of sulfide oxidation by hydrogen peroxide rise to a big extent; (4) the % solid generate during oxidation reaction was decreased through reaction time and turbidity working solution was pale during oxidation for all variation, the % solid at 10 – 15

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minutes were higher sodium solid formed, that are sulphur, Na_2SO_4, $Na_2S_2O_3$, $Na_2S_3O_6$, etc; and (5) The effect of the initial and oxidation pH value of sulphide waste on the total sulphide removal by the oxidation reaction was studied in the pH range of 7 to 11 for initial pH to adjust the pH value reaction and 3.5 to 9 by adding H_2O_2 as proceeds oxidation. The results of this study are expected to be useful for assessment of alternatives and to utilize sulfide waste by transferring the NaSH treatment process to processing in other chemical industries. Therefore, a solution is needed to reduce and utilize sulfide waste by carrying out the oxidation method as a step to produce new commodity products that can be utilized by industries that produce sulphide waste or become a new product share to increase the added value of sulfide waste.

Acknowledgements

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