

STUDY OF EFFICIENCY AND REACTION RATES DECHLORINATION OF NATA DE COCO WASTEWATER USING SODIUM THIOSULFATE

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Abstract

Chemical reduction with sodium thiosulfate is commonly used to dechlorinate chlorinated waste. U.S. Environmental Protection Agency recommends sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) as a dechlorinating agent for waste samples containing residual chlorine before being released into the environment or entering the distribution system. However, sodium thiosulfate's efficiency and chlorination kinetics at different concentrations are still unknown due to a lack of information on chlorination kinetics. The study was conducted by determining the number of efficient doses of sodium thiosulfate and observing chlorination kinetics using sodium thiosulfate as a dechlorination agent observed at different stoichiometric ratios (1x, 1.5x, and 2x). Sodium thiosulfate at a stoichiometric dose of 2x can reduce chlorine residue by up to 0.4 ppm. The regression analysis of and constant rate are used in the kinetic analysis of sodium thiosulfate dechlorination processes. The kinetics of the chlorination process employing sodium thiosulfate is first order to the total concentration of chlorine in solution at a stoichiometric dosage of 2x, according to the findings.

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1. Introduction

Indonesia is one of the largest producers and exporters of agricultural products globally. In recent years, the agricultural industry has also been the largest employment sector in the country [1]. Indonesia's economic growth is primarily driven by increasing household consumption and one of the rapidly growing industries in the food industry. One of the food sectors that have high demand in the South East Asia region is the nata de coco industry [2]. This industry, which uses agricultural products as its principal raw material, is one example of an agro-industrial. The increasing public need for nata de coco products provides benefits to the economy, but on the other hand, causes various side effects due to its waste.

Waste generated from nata de coco production, that utilizes microbes in the process, is the emergence of environmental problems, namely increasing the value of biochemical oxygen demand (BOD) [3]. The high BOD value indicates that the wastewater contains a lot of pollutant organic substances. Pollution by organic substances will result in the death of aquatic biota because oxygen needs are used for the decomposition process, and water conditions that lack oxygen levels (anaerobic) will cause a bad smell [4]. The high level of pollutant content in the waste causes the nata de coco industry not to be able to dispose of its waste to the environmental agency directly. Appropriate technology is needed to treat the waste so that the treated water can meet the acceptable environmental quality standards. So to reduce the environmental impact, it takes a proper way to treat waste before it is discharged into the environment, which will later be passed on to water bodies to prevent water pollution that can harm to environment.

In general, the waste treatment system consists of the primary process stages, namely coagulation, flocculation, sedimentation, aeration, filtration, and disinfection [5]. The process of disinfection processing that is often used is the establishment of chlorine into waste, or called the chlorination process. Chlorination is a disinfection process used in water and wastewater treatment to control the amount of microbial contamination in water [6]. The chlorination process is often used as an alternative to the processing process because of (i) relatively low cost, (ii)

high efficiency, and (iii) ease of use [7]. The efficiency of chlorination largely depends on the chemicals used. In the process, chlorine is usually used in the form of chlorine gas (Cl_2), sodium hypochlorite (NaOCl), and Calcium Hypochlorite ($\text{Ca}(\text{OCl})_2$) [8].

Because of its strong disinfectant power and inexpensive cost, chlorine is a commonly used as disinfectant agent for waste treatment process [9]. However, the amount of chlorine added varies significantly depending on the organic content of the water to be treated [10], [11]. In wastewater treatment processes, chlorine is often given beyond the theoretical dose needed to ensure the disinfection process meets industrial needs [12], [13]. Due to the process of disinfection of the resulting water consistently producing chlorine residues, the high levels of chlorine residues cause a special odor produced from chlorine and will interfere with the respiratory system when inhaled in large quantities. The resulting water always produces chlorine residues and byproducts that are toxic to aquatic organisms and cause the death of organisms that will damage the aquatic ecosystem and loss of species diversity [14]. Accumulating evidence about the toxicity of residual chlorine in wastewater effluent has led to the implementation of stronger regulations or guidelines to minimize the discharge of residual chlorine in the final effluent stream. Higher amounts of residual chlorine can be reduced before effluent water is discharged into the environment and distributed to distribution systems [15].

In this regard, to minimize excessive chlorine residues in wastewater before the wastewater is released into the environment for system distribution, high levels of chlorine residue can be reduced by the addition of reducing substances that will convert chlorine into less harmful chloride [16]. The process of removing residual chlorine from disinfecting waste before it is discharged into the environment is referred to as dechlorination. The goal of the dechlorination process is to reduce all chlorine-produced oxidants to a non-reactive halide form through a chemical reaction [17]. Sulfur dioxide, sodium bisulphite (NaHSO_3), sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) have been used as dechlorinating agent (DA) in the chemical dechlorination process [18].

Dechlorination agents are used to decrease chlorine's impact on aquatic life. As a result, a dechlorination agent that is least harmful to aquatic life is chosen [19]. The selection of methods and dechlorination compounds will affect the removal of chlorine residues. Several studies have used sulfur compounds as chlorine removal media in wastewater treatment. Several DA have been studied for their effectiveness for aquatic life, Nweke et al. suggests that dechlorination of liquid waste with S-IV compounds may be incomplete [17]. This incomplete dechlorination can leave high chlorine residues and threaten aquatic ecosystems if discharged into the environment. Another study conducted by Basu et al. showed that the use of sodium thiosulfate in dechlorination would decrease the value of TOC or Total Organic Compound to not cause the death of the water ecosystem. It suggests that sodium thiosulfate is not toxic or toxic to aquatic organisms [20], [21]. Oh, et al. used sodium thiosulfate in the dechlorination of wastewater containing several chlorine residues in their study [22]. The dechlorination procedure in flowing water using sodium thiosulfate capable of eliminating chlorine up to 0.5 ppm was also documented in Adeyemo et al's work [23]. Furthermore, another study found that using sodium thiosulfate in the dechlorination of wastewater might minimize the toxicity of metals present [24]. Also, sodium thiosulfate is one of the most commonly used dechlorination agents [25]. The results show that sodium thiosulfate as a dechlorination agent has good potential in efforts to handle chlorine-containing waste in high concentrations. Research conducted in the 1950s recommended using sodium thiosulfate into waste samples to be dechlorinating because it effectively neutralizes residual chlorine derived from pipeline distribution [26]. Its availability in tablet form makes sodium thiosulfate have a shelf life of about one year.

The effect of sodium thiosulfate in dechlorinating effluent from the Nata de Coco waste will be investigated in this study. Residual chlorine concentration target after treatment using $\text{Na}_2\text{S}_2\text{O}_3$ is 0.5 ppm following the Decree of the State Minister of the Environment of Indonesia [27]. The numerous additions of dechlorination agents, pH, and the final concentration of the sample after dechlorination all impact the efficiency of sodium thiosulfate. Furthermore, there is a limited publication on the kinetics of dechlorination agent-chlorine reactions at varied dosages and pH levels. Especially in the use of sodium thiosulfate as a dechlorination agent. In order to undertake this research, laboratory experiments will be used to explore and evaluate the reaction rates of numerous dechlorination agents with chlorine in municipal wastewater. Under a variety of dose and pH conditions, these tests looked at the pace and efficiency of dechlorination in terms of reaction time.

2. Experimental

2.1. Monitoring of Dechlorination

Waste samples were obtained from the nata de coco industry at Banten, Indonesia. The measurement using Dulcometer DIC shows that the waste sample has chlorine residue levels of 50 ± 0.2879 mg/L. All experiments

were conducted in the pH range of 6, 7, and 9. Sulfuric acid (H₂SO₄) was used to lower the pH, and sodium hydroxide (NaOH) was used to increase the pH of the sample solution. For instance, to control pH at 6, 0.20 mL H₂SO₄ was added into the solution while pH 9 was achieved by 0.15 mL NaOH addition. This pH range was selected to meet the common pH value in most treated wastewater effluents, whereas the pH range 9 was chosen to simulate the scenario where the pH is slightly over the higher margin of the typical pH range of wastewater.

The amount of chlorine residue is checked periodically every 15 min to ensure the amount of chlorine residue has met the minimum requirement. The waste samples used for one experiment amounted to 50 mL. The test solution is mixed with a magnetic stirrer to mix the dechlorination agent sodium thiosulfate. Dechlorination process is considered to be completed after the total chlorine level is below 0.5 mg/L. Each dechlorination experiment is divided into several variations of the Na₂S₂O₃ addition method, that is addition according to stoichiometry (1 × STS or 1x), 1.5 times the stoichiometric addition (1.5 × STS or 1.5x), and 2 times the stoichiometric addition (2 × STS or 2x).

Reaction equations during dichlorination process are given as follows [28]:



The required stoichiometric dosages for Sodium Thiosulfate (STS) were calculated according to the chemical reaction equations. Calculation of the number of Sodium Thiosulfate (STS) [28]:

$$\frac{158.1 \text{ mg } Na_2S_2O_3}{2 \text{ mol } Na_2S_2O_3} \times \frac{2 \text{ mol } Na_2S_2O_3}{1 \text{ mol } HOCl} \times \frac{1 \text{ mol } HOCl}{52.46 \text{ mg } HOCl} = 3.013 \text{ mg STS} / \text{mg } HOCl \quad (2)$$

Stoichiometric dosage required of dechlorination agent to neutralize 1 mg of HOCl residual in solution for each variation stoichiometry (1x, 1.5x, and 2x) was 3.012 mg, 4.516 mg, and 6.026 mg.

2.2. Linear Regression

Linear Regression or graphical method was done to determine the kinetic reaction with regard to the reactant concentration, three plots are made. The first is concentration of the dechlorinating agent versus time. The second is the inverse concentration versus time, while the third is of the natural log of concentration versus time. These graphs, respectively, show zero, first, and second order dependence on the specific reactant. We can observe that the plot according to any of these plots is linear and it shows the order of reaction [29].

The coefficient of determination is the portion of the total variation in the dependent variable that can be explained by variation in the independent variable. The multiple correlation coefficient, which is often denoted by R, is the square root of the coefficient of determination. Those coefficient has the value between 0 and 1. When R² is close to 1, there exists a perfect linear relationship between x and y of the variation in y is explained by variation in x. When it is 0 < R² < 1, there is a weaker linear relationship between x and y. In the linear regression with only one explanatory variable (x), R is equal to the absolute value of the correlation coefficient r between x and the objective variable (y) [30].

2.3. Dechlorination Rates

There are two types of analysis of kinetic data; the differential rate law shows how the reaction rate depends on concentration, while integrated rate law shows how the concentration of species in reactions depends on time [31]. In this experiment, the concentration of reactants was measured as a function of time, so this data helped determine the integrated rate law (concentration vs. time) for each stoichiometric ratio. The integrated rate law used for each reaction depends on the type of reaction being considered. The data is analyzed using integral methods because this method is proper when adjusting a simple type of reaction that corresponds to an elementary reaction and depends on the kinetic shape of the reaction [32]. Integral approaches are very straightforward to apply and are recommended when assessing rates that are quite simple. Because differential approaches need a huge quantity of data, they are hardly employed. The model regression approach will be utilized to determine the response rate using previously collected data. To explore the sequence of the reaction, a plot was produced for each from a dosage of stoichiometry.

$$2.3.1 \text{ Zero order kinetics : } -r = k \\ C_A = -kt + C_0 \quad (3)$$

Thus,

$$t = \frac{1}{k} (C_0 - C_A) \quad (4)$$

Where k = rate constant; t = times; and C_A = concentration of the free chlorine species.

Total chlorine (C) concentration versus time was plotted, and if it yields a straight line, the slope (k) represents the rate constant. For zero-order reactions, the rate is constant, and it does not change with concentrations as it does for first-order or second-order reactions [28].

$$\begin{aligned} 2.3.2 \text{ First-order kinetics: } -r_A &= kC_A \\ [C_A] &= [C_0] \times e^{-k} \times t \end{aligned} \quad (5)$$

$$-\ln \frac{C_A}{C_0} = kt \quad (6)$$

Thus,

$$t = \left(\frac{1}{k}\right) \ln \frac{C_A}{C_0} \quad (7)$$

In this case, the plot of $\ln \left(\frac{C_A}{C_0}\right)$ versus time gives the straight line, where the slope ($-k$) represents the rate constant.

$$\begin{aligned} 2.3.3 \text{ Second-order kinetics : } -r_A &= kC_A^2 \\ C_A &= -k \times t \end{aligned} \quad (8)$$

$$\frac{1}{C_A} = kt + \frac{1}{C_0} \quad (9)$$

Thus,

$$t = \frac{1}{k} \left(\frac{1}{C_A} - \frac{1}{C_0}\right) \quad (10)$$

In this case, the plot of $\frac{1}{C}$ versus time gives a straight line where the slope (k) represents the rate constant.

The R^2 value for the line is best suited for all data points compared between plots to infer the sequence of reactions for each dechlorination agent. The plot is also visually investigated to assess the most suitable. The plot with the highest R^2 value is selected to produce the best match, and the reaction order is precisely assigned.

3. Result and Discussion

3.1. Chlorine Residual Analysis

Indonesia regulation require that wastewater discharged by the environment must meet environmental quality standards, especially the number of chlorine residues state in Liquid Waste Quality Standards for Industrial Activities of the maximum allowed chlorine residue levels of 0.5 mg/L (Decree of the State Minister of the Environment no KEP-51/MENLH/10/1995) [27]. This regulatory makes its standard for each industrial activity in the waste disposal regulation with the recommended chlorine limit. In Indonesia, dechlorination is not yet commonly used, so there is no adequate literature in determining chlorine residue levels before being discharged into the distribution system. Thus, the maximum limit used following the rules of the Ministry of Environment, which is 0.5 mg/L [33]. The condition of the waste dechlorination process (pH and temperature) in this study are kept constant at pH 6, 7, and 9 and temperatures of 25°C. The selection of the pH range used during the dechlorination process is based on the rules of the Ministry of Environment which explains that the maximum pH value allowed in waste disposal is 6 – 9 [27].

Sodium thiosulfate (STS) dechlorination is not complete utilizing 1x stoichiometry, and reaction time is slower than sodium bisulfite (SBS) with ascorbic acid (AA), according to previous research [34]. Another research has found that dechlorination is a relatively long period (1 hour reaction) [24]. Inconsistent data in existing literature may be partly due to different expectations of residual chlorine from water and wastewater treatment plants.

Therefore, the study of the completeness of the reaction can be different due to the target amount of chlorine residue to be achieved in the wastewater. Furthermore, past studies of the quantity of chlorine contained in waste differed, affecting reaction timeframes and the desired residual levels of chlorine, as well as the reaction's completeness [15], [24].

Fig. 1 compares all dechlorination reactions at 1x, 1.5x, and 2x stoichiometric dosage. This figure shows that in the case of STS the reaction is not complete. Compared to previous studies by Weerasinghae et al., using STS as a Dechlorination Agent (DA), the use of STS is complete on reaction at 2, 3, and 10x stoichiometric dosage reactions complete in 40 - 60s [28]. However, this study on reaction 2x stoichiometric dosage was incomplete because it did not reach residual chlorine levels up to 0.5 mg/L. Some previous studies conducted experiments on wastewater samples with levels of 1.5-2 mg/L with a reaction time of 180 seconds [28], other study, using running water with chlorine residue levels of 0.5 mg/L and mentioned the reaction using STS as a DA occurred quickly [34]. The complete removal of total residual chlorine was achieved using a 3x stoichiometric dosage of STS and the reaction time was 75 – 100 seconds on the study using trial sample concentration of 2 mg/L [15], [28]. This difference can be due to different types of waste, and the amount of initial chlorine residue levels are different. The amount of chlorine residue remaining in the waste will take more time and more DA.

The total chlorine residual illustrated in Fig. 1 suggests that the residual chlorine decreases as stoichiometry dosage increases. A high amount of reagent increases the dechlorination rate so that the residual chlorine is less. Treatment of the dechlorination process using $\text{Na}_2\text{S}_2\text{O}_3$ in acidic, neutral, and alkaline conditions reduced residual chlorine from a concentration of 50 ppm to less than 1 ppm. The decrease in chlorine residue levels for 180 min was at most achieved by samples with a pH of 6, while at pH 7 and 9 the decrease in chlorine residues was less than the maximum because it was still above the concentration of 0.5 ppm. In figure 1(a) of a sample with a pH of 6, chlorine levels at the initial concentration of 50 ppm drop to 3 ppm within the first 15 min. It then drops significantly every 15 min until it reaches a concentration of 0.5 ppm. In addition, at pH 9 in the first 15 min the concentration of chlorine residues did not decrease in pH 9.

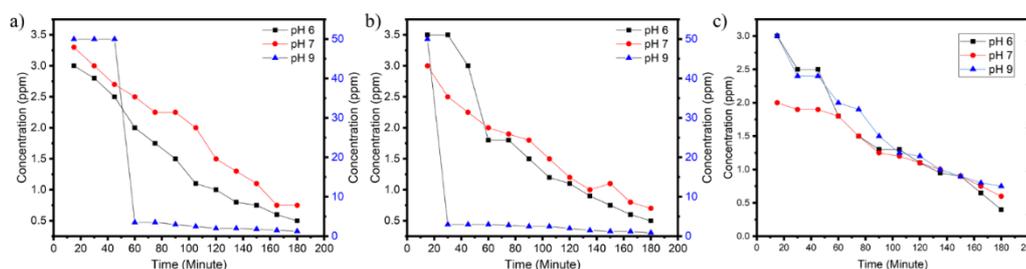


Figure 1. Comparison of dechlorination result profiles at (a) 1x, (b) 1.5x, (c) 2x stoichiometry

At a ratio of 1.5x stoichiometry sodium thiosulfate as a chlorinated agent in a 50 mL waste sample showed less chlorine residue than 1x stoichiometry. The effect of increasing the amount of sodium thiosulfate into the sample against the decrease in chlorine levels greatly affects the maximum amount of chlorine residue that can be produced during the 180 min process time. The more sodium thiosulfate added, the less chlorine residue remains in the sample. It can be seen in Figure 1(b) above, for 180 min all samples in different pH ranges produce residual chlorine residue levels below 1 ppm. When compared to the remaining chlorine residue levels of 1x stoichiometry results above are much better. However, pH 7 and pH 9 still do not meet environmental quality standards. So it has not reached the process of dechlorination properly.

In the treatment of 2x stoichiometry of sodium thiosulfate, the results obtained from the addition of 2x stoichiometry are better than the addition of 1.5 times stoichiometry, the more $\text{Na}_2\text{S}_2\text{O}_3$ added, the less residual chlorine contained in the waste. The effect of the addition of $\text{Na}_2\text{S}_2\text{O}_3$ on decreasing residual chlorine is shown in Figure 1 (c) for 180 min the remaining chlorine residue reaches 0.4 ppm in acidic conditions and in alkaline conditions it can reach 0.7 ppm. The graph shows a very significant decrease every 15 min compared to the stoichiometry of $\text{Na}_2\text{S}_2\text{O}_3$ 1x and 1.5x at pH 9, the first 15 min was able to reduce residual chlorine from 50 ppm to 3.5 ppm. When compared with the previous treatment, in the first 15 min of the sample with a pH of 9, there was no decrease in the residual chlorine. The more the amount of sodium thiosulfate added, the less residual chlorine content is left in the sample.

Results from laboratory experiments indicate that chlorine concentration decreased upon addition Stoichiometric dose and decreased when the pH sample was 6. Research conducted by Basu et al., showed that the reaction in the dechlorination process using $\text{Na}_2\text{S}_2\text{O}_3$ in acidic conditions reduced the residual chlorine up to 0.12 ppm faster [34]. The lower the pH, the less residual chlorine content, on the contrary, the higher the pH, the higher the residual chlorine content. This is due to the presence of organic and inorganic components in the sample. The presence of organic and inorganic components in the waste will inhibit the dechlorination process so that the dechlorination process is not optimal [34]. The process of chlorination basically will increase the pH of the water to a neutral pH, but it is possible that there will still be organic and inorganic components remaining. The presence of organic and inorganic components allows the presence of bacteria in the waste, the pH is effective for killing bacteria at low pH (acidic) conditions. Therefore, in the dechlorination condition, the acid pH treatment has very little residual chlorine content and meets the environmental quality standards.

The reaction of calcium hypochlorite ($\text{Ca}(\text{OCl})_2$) in water will form hypochlorous acid (HOCl), where hypochlorous acid will decompose into H^+ and OCl^- ions. This reaction is very dependent on the pH of the solution, when the pH of the solution is alkaline, the reaction will shift to the right so that more hypochlorite ions (OCl^-) will be formed, so that in alkaline conditions the dechlorination process is less effective due to bacteria or microorganisms or organic and non-organic components. still in wastewater. In addition, bacterial cells are generally negatively charged, if in an alkaline state they form hypochlorite ions (OCl^-) then bacteria will not interact with hypochlorite ions because they have the same charge. Conversely, if the pH of the solution is acidic, the reaction will shift to the left so that more hypochlorous acid is formed. The strength of hypochlorous acid is generally stronger and faster in the process of removing microorganisms and organic and non-organic content in the waste than the hypochlorous ion. So that the dechlorination process will achieve a complete reaction at an acidic pH.

The addition of a dose of $\text{Na}_2\text{S}_2\text{O}_3$ in this study resulted in the least residual chlorine residue. Alternatively, other words, by adding $\text{Na}_2\text{S}_2\text{O}_3$, the dechlorination process became more effective than without the addition of $\text{Na}_2\text{S}_2\text{O}_3$. This result follows an experimental study in the literature [35]. It was found that the addition of a dechlorinating agent dose of 2x the stoichiometric dose was able to reduce the residual chlorine level more. In addition, STS in his research to achieve complete dechlorination was minimally carried out by adding 1.5x the dose of $\text{Na}_2\text{S}_2\text{O}_3$. Theoretically, increasing the dose of $\text{Na}_2\text{S}_2\text{O}_3$ is more effective than without addition. These results have good agreement with previous studies result. In his study, Worley et al. mention that STS can remove chlorine at twice the dose of stoichiometry. The experiment was conducted in a solution with an acidic pH. In addition, in his study, STS reportedly required several times the stoichiometric dose (at least 1.5x) to achieve complete dechlorination [36].

3.2. Dechlorination Reaction Rate Analysis

Three different regression models, zero-order, first-order and second-order reaction, were applied to each stoichiometric ratio to determine which order is appropriate by comparing the dechlorination profile, i.e., time and specified concentration. Theoretically, the order will shift from high order to a lower order or a zero-order reaction rate along with an increase in the dose of stoichiometry. It should be noted that this analysis is based on the best fit.

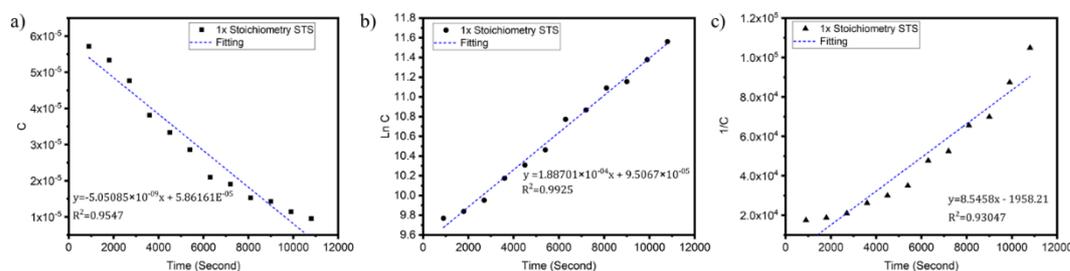


Figure 2. Regression curves for STS at 1x stoichiometry (a) zero-, (b) first-, (c) second-order kinetics

Fig. 2 showing the results of regression patterns for STS at 1x stoichiometry, the zero-order reaction chart shows the value of R^2 0.9547 with a constant reaction rate of $0.0159 \text{ M}\cdot\text{s}^{-1}$. On the first-order reaction chart, the value of R^2 is more excellent, which is 0.9925. This value is close to 1, and the reaction rate is 0.113 s^{-1} . While on the second-order chart, the value of R^2 is 0.8305 with a reaction rate of $0.0098 \text{ M}^{-1}\cdot\text{s}^{-1}$. The value of R^2 at 1x

stoichiometry is close to 1 on the first-order reaction chart, indicating that regression is suitable against the first-order reaction. The results reported in the results of previous studies showed that STS at a stoichiometric ratio of 1x did not reach zero-order [28]. At DA doses of 1.5x stoichiometry (Figure 3), zero-order, first-order, and second-order reaction charts show consecutive R^2 values of 0.8969, 0.9836, and 0.9206. Judging from the value of R^2 in the first-order reaction, showing at DA 1.5x stoichiometry, the results are suitable for a first-order reaction.

Similarly, a DA dose of 2x stoichiometry, Fig. 4 shows the most suitable R^2 value in the first-order reaction of 0.9524. When the dose is raised by 1.5x stoichiometry, the results match the first-order reaction. At stoichiometric doses of 1.5x and 2x in previous studies reported that at doses of more than 1x, the reaction would indicate first-order reaction, with the doses used being 2x, 4x, and 10x stoichiometry [28].

In first-order reaction, the reaction rate of 1x and 1.5x stoichiometry doses decreases from 0.113 to 0.0122 s^{-1} . Similarly, at a dose of 2x stoichiometry, the R^2 value indicates that a stoichiometric dose of 2x fits against the first-order reaction. Similarly, the reaction rate constant in stoichiometry 2x decreased to 0.0106 s^{-1} . This suggests that increasing the amount of added sodium thiosulfate does not increase the reaction rate substantially. Generally, the overall reaction rate constant will increase with the increase in the number of DA doses added. Deviations, in this case, may be caused by the presence of dissolved oxygen in the sample and chlorine for reduction by the dechlorination agent because sulfite is a source of electrons for the reduction of hypochlorite compounds in waste [15], [37]. Table 1 shows k-values and Corresponding R^2 obtained for all stoichiometry dosages.

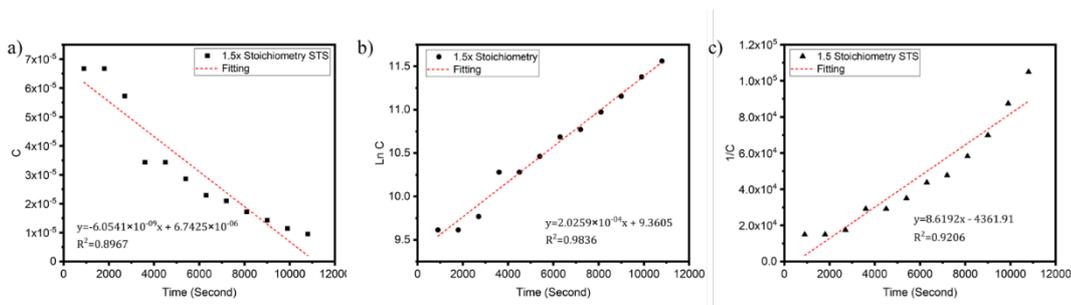


Figure 3. Regression curves for STS at 1.5x stoichiometry (a) zero-, (b) first-, (c) second-order kinetics

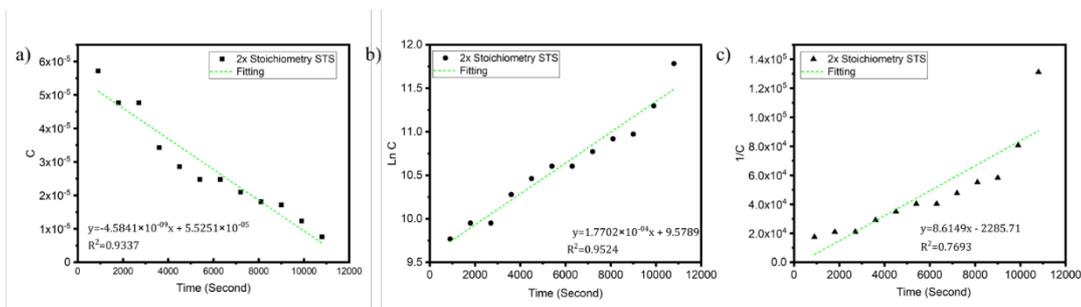


Figure 4. Regression curves for STS at 2x stoichiometry (a) zero-, (b) first-, (c) second-order kinetic.

Table 1. k-values and Corresponding R² obtained for all stoichiometry dosages (1x, 1.5x, and 2x)

Dechlorination Chemical Dosages	Zero-order Regression		First-order Regression		Second-order regression	
	k (M.s ⁻¹)	R ²	k (s ⁻¹)	R ²	k (M ⁻¹ .s ⁻¹)	R ²
1 × STS	0.0159	0.9547	0.113	0.9925	0.0098	0.8305
1.5 × STS	0.0191	0.8969	0.0122	0.9836	0.0099	0.9206
2 × STS	0.0144	0.9337	0.0106	0.9524	0.0099	0.7693

4. Conclusions

This study focused on the rate and the efficiency of dechlorination, concerning reaction time, under a range of dosages and pH at three different stoichiometric ratios. Under the conditions of this research, one of the three dechlorination dosages was found to be reducing chlorine residue levels in industrial liquid waste nata de coco from 50 ppm to 0.4 ppm in waste conditions with a pH of 6. So it deserves to be thrown into the environment because it has met the environmental quality standards. Other test parameters have been examined in this study, namely the reaction order at three different stoichiometry, these results have confirmed that the most suitable reaction order at stoichiometric doses of 1x, 1.5x, and 2x is the first-order reaction.

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References

- [1] OECD, "Agricultural Policy Monitoring and Evaluation 2021." OECD, Jun. 22, 2021. doi: 10.1787/2d810e01-en.
- [2] M. Phisalaphong *et al.*, "Nata de coco Industry in Vietnam, Thailand, and Indonesia," in *Bacterial Nanocellulose*, M. Gama, F. Dourado, and S. B. T.-B. N. Bielecki, Eds. Amsterdam: Elsevier, 2016, pp. 231–236. doi: 10.1016/B978-0-444-63458-0.00014-7.
- [3] C. K. Venil, P. R. Devi, and W. A. Ahmad, "Agro-Industrial Waste as Substrates for the Production of Bacterial Pigment," in *Valorisation of Agro-industrial Residues – Volume I: Biological Approaches*, Z. A. Zakaria, R. Boopathy, and J. R. Dib, Eds. Cham: Springer International Publishing, 2020, pp. 149–162. doi: 10.1007/978-3-030-39137-9_7.
- [4] A. J. Englande, P. Krenkel, and J. B. T.-R. M. in E. S. and E. S. Shamas, "Wastewater Treatment & Water Reclamation," in *Reference Module in Earth Systems and Environmental Sciences*, Elsevier, 2015. doi: https://doi.org/10.1016/B978-0-12-409548-9.09508-7.
- [5] C. Y. Teh, P. M. Budiman, K. P. Y. Shak, and T. Y. Wu, "Recent Advancement of Coagulation–Flocculation and Its Application in Wastewater Treatment," *Ind. Eng. Chem. Res.*, vol. 55, no. 16, pp. 4363–4389, 2016, doi: 10.1021/acs.iecr.5b04703.
- [6] J. Zheng, C. Su, J. Zhou, L. Xu, Y. Qian, and H. Chen, "Effects and mechanisms of ultraviolet, chlorination, and ozone disinfection on antibiotic resistance genes in secondary effluents of municipal wastewater treatment plants," *Chem. Eng. J.*, vol. 317, pp. 309–316, 2017, doi: https://doi.org/10.1016/j.cej.2017.02.076.
- [7] S. Saby, M. Djafer, and G.-H. Chen, "Feasibility of using a chlorination step to reduce excess sludge in activated sludge process," *Water Res.*, vol. 36, no. 3, pp. 656–666, 2002, doi: https://doi.org/10.1016/S0043-1354(01)00259-7.
- [8] Y. Choi, S.-H. Byun, H.-J. Jang, S.-E. Kim, and Y. Choi, "Comparison of disinfectants for drinking water: chlorine gas vs. on-site generated chlorine," *Environ. Eng. Res.*, vol. 27, no. 1, pp. 200540–200543, 2022, doi: 10.4491/eer.2020.543.
- [9] A. Arjoon, A. O. Olaniran, and B. Pillay, "Co-contamination of water with chlorinated hydrocarbons and heavy metals: challenges and current bioremediation strategies," *Int. J. Environ. Sci. Technol.*, vol. 10, no.

- 2, pp. 395–412, 2013, doi: 10.1007/s13762-012-0122-y.
- [10] M. C. Collivignarelli, A. Abbà, I. Benigna, S. Sorlini, and V. Torretta, “Overview of the Main Disinfection Processes for Wastewater and Drinking Water Treatment Plants,” *Sustainability*, vol. 10, no. 1, p. 86, 2018, doi: 10.3390/su10010086.
- [11] E. Friedler, D. F. Chavez, Y. Alfiya, Y. Gilboa, and A. Gross, “Impact of Suspended Solids and Organic Matter on Chlorine and UV Disinfection Efficiency of Greywater,” *Water*, vol. 13, no. 2, p. 214, 2021, doi: 10.3390/w13020214.
- [12] C. Goodburn and C. A. Wallace, “The microbiological efficacy of decontamination methodologies for fresh produce: A review,” *Food Control*, vol. 32, no. 2, pp. 418–427, 2013, doi: <https://doi.org/10.1016/j.foodcont.2012.12.012>.
- [13] A. Withers, “Options for recarbonation, remineralisation and disinfection for desalination plants,” *Desalination*, vol. 179, no. 1, pp. 11–24, 2005, doi: <https://doi.org/10.1016/j.desal.2004.11.051>.
- [14] E. Lakshmi, M. Priya, and V. S. Achari, “An overview on the treatment of ballast water in ships,” *Ocean Coast. Manag.*, vol. 199, p. 105296, 2021, doi: <https://doi.org/10.1016/j.ocecoaman.2020.105296>.
- [15] B. M. Hermant and O. D. Basu, “Comparison of Reaction Rates and Relative Efficiencies for Various Dechlorination Chemicals,” *J. Environ. Eng.*, vol. 139, no. 4, pp. 522–529, 2013, doi: 10.1061/(asce)ee.1943-7870.0000544.
- [16] H.-L. Lien and W. Zhang, “Nanoscale iron particles for complete reduction of chlorinated ethenes,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 191, no. 1, pp. 97–105, 2001, doi: 10.1016/S0927-7757(01)00767-1.
- [17] G. R. Helz and A. C. Nweke, “Incompleteness of Wastewater Dechlorination,” *Environ. Sci. Technol.*, vol. 29, no. 4, pp. 1018–1022, 1995, doi: 10.1021/es00004a023.
- [18] M. J. Brandt, K. M. Johnson, A. J. Elphinston, and D. D. Ratnayaka, “Disinfection of Water,” in *Twort’s Water Supply*, 7th ed., M. J. Brandt, K. M. Johnson, A. J. Elphinston, and D. D. Ratnayaka, Eds. Boston: Butterworth-Heinemann, 2017, pp. 475–511. doi: <https://doi.org/10.1016/B978-0-08-100025-0.00011-9>.
- [19] B. N. Weerasinghe, “Kinetics of tap water dechlorination and aquatic health impacts of selected dechlorination chemicals,” Carleton University, 2008. doi: 10.22215/etd/2008-08181.
- [20] M. A. Giles and R. Danell, “Water Dechlorination By Activated Carbon, Ultraviolet Radiation And Sodium Sulphite A Comparison Of Treatment Systems Suitable For Fish Culture,” *Water Res.*, vol. 17, no. 6, pp. 667–676, 1983, doi: 10.1016/0043-1354(83)90236-1.
- [21] A. Sathasivan, B. S. Herath, S. T. M. L. D. Senevirathna, and G. Kastl, “Dechlorination in Wastewater Treatment Processes,” in *Current Developments in Biotechnology and Bioengineering*, L. Duu-Jong, J. Veeriah, H. N. Hao, P. C. Hallenbeck, and A. Pandey, Eds. Elsevier Inc., 2017, pp. 359–380. doi: 10.1016/B978-0-444-63665-2.00014-X.
- [22] S. R. Oh, J. K. Kim, M. J. Lee, and K. Choi, “Dechlorination with sodium thiosulfate affects the toxicity of wastewater contaminated with copper, cadmium, nickel, or zinc,” *Environ. Toxicol.*, vol. 23, no. 2, pp. 211–217, 2008, doi: 10.1002/tox.20325.
- [23] F. E. Adeyemo, G. Singh, P. Reddy, F. Bux, and T. A. Stenström, “Efficiency of chlorine and UV in the inactivation of *Cryptosporidium* and *Giardia* in wastewater,” *PLoS One*, vol. 14, no. 5, p. e0216040, 2019, doi: 10.1371/journal.pone.0216040.
- [24] W. A. MacCrehan, M. Bedner, and G. R. Helz, “Making chlorine greener: Performance of alternative dechlorination agents in wastewater,” *Chemosphere*, vol. 60, no. 3, pp. 381–388, 2005, doi: 10.1016/j.chemosphere.2004.11.075.
- [25] A. L. Murray, E. Kumpel, R. Peletz, R. S. Khush, and D. S. Lantagne, “The effect of sodium thiosulfate dechlorination on fecal indicator bacteria enumeration: laboratory and field data,” *J. Water Health*, vol. 16, no. 1, pp. 44–48, 2018, doi: 10.2166/wh.2017.077.
- [26] R. C. Hoather, “The Effect Of Thiosulphate And Of Phosphate On The Bactericidal Action Of Copper And Zinc In Samples Of Water,” *J. Appl. Bacteriol.*, vol. 20, no. 2, pp. 180–187, 1957, doi: 10.1111/j.1365-2672.1957.tb00090.x.
- [27] “Baku Mutu Limbah Cair Bagi Kegiatan Industri,” *Kep. Men. Neg. LH No.: KEP-51/MENLHI1011995*. 1995.
- [28] O. D. Basu and B. N. B. N. Weerasinghe, “Comparison of reaction kinetics under varying conditions for dechlorination chemicals,” in *Proceedings of the Water Environment Federation*, 2008, pp. 1922–1931. doi: 10.2175/193864708788734025.
- [29] K. A. Connors, *Chemical Kinetics: The Study of Reaction Rates in Solution*. John Wiley & Sons, Inc., 1990.
- [30] E. Kasuya, “On the use of r and r squared in correlation and regression,” *Ecol. Res.*, vol. 34, no. 1, pp. 235–236, Jan. 2019, doi: <https://doi.org/10.1111/1440-1703.1011>.

- [31] R. Grima, "An effective rate equation approach to reaction kinetics in small volumes: Theory and application to biochemical reactions in nonequilibrium steady-state conditions," *J. Chem. Phys.*, vol. 133, no. 3, p. 35101, Jul. 2010, doi: 10.1063/1.3454685.
- [32] D. E. Meyer and D. Bhattacharyya, "Impact of Membrane Immobilization on Particle Formation and Trichloroethylene Dechlorination for Bimetallic Fe/Ni Nanoparticles in Cellulose Acetate Membranes," *J. Phys. Chem. B*, vol. 111, no. 25, pp. 7142–7154, 2007, doi: 10.1021/jp070972u.
- [33] N. Rohmah, D. Roosmini, and M. A. Septiono, "Study of whole effluent acute toxicity test (*Daphnia magna*) as an evaluation of Ministry of Environment and Forestry Decree No. 3 In 2014 concerning industrial performance rank in environmental management," in *MATEC Web of Conferences*, 2018, vol. 147, p. 08005. doi: 10.1051/mateconf/201814708005.
- [34] O. D. Basu and N. P. De Souza, "Comparison of dechlorination rates and water quality impacts for sodium bisulfite, sodium thiosulfate and ascorbic acid," *J. Water Supply Res. Technol. - Aqua*, vol. 60, no. 3, pp. 167–177, 2011, doi: 10.2166/aqua.2011.040.
- [35] R. L. Wolfe, N. R. Ward, and B. H. Olson, "Inorganic chloramines as drinking water disinfectants: A review," *J. Am. Water Works Assoc.*, vol. 76, no. 5, pp. 74–88, 1984, doi: 10.1002/j.1551-8833.1984.tb05337.x.
- [36] J. L. Worley, A. M. Dietrich, and R. C. Hoehn, "Dechlorination techniques to improve sensory odor testing of geosmin and 2-MIB," *J. Am. Water Works Assoc.*, vol. 95, no. 3, pp. 109–117, Mar. 2003, doi: 10.1002/j.1551-8833.2003.tb10319.x.
- [37] T. R. Chaparro and E. C. Pires, "Anaerobic treatment of cellulose bleach plant wastewater: chlorinated organics and genotoxicity removal," *Brazilian J. Chem. Eng.*, vol. 28, pp. 625–638, 2011, doi: 10.1590/S0104-66322011000400008.

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