Application of the Fenton Process in the Petroleum Refinery Spent Caustic Wastewater Treatment

Riang Anggraini Rahmanisa[1], I Nyoman Widiasa[1, *]

[1]Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro
Jl. Prof. Soedarto, SH, Tembalang, Semarang

[*]Corresponding author: widiasa@che.undip.ac.id

Abstract

Spent caustic wastewater is produced from the scrubbing process using a caustic solution to absorb contaminants in the oil stream (hydrocarbon). Indonesia's Petroleum Oil Refinery produces spent caustic wastewater from LPG and kerosene processing unit. Spent caustic wastewater has the characteristic of a strong odor with very high pH (12-14), containing dangerous pollutants such as phenol, aldehydes, mercaptans, and thiols that can be harmful to the human and environment. The Fenton process is used to treat spent caustic before being discharged to the environment. The Fenton process is one of AOPs (Advanced Oxidation Process) using Fe^{2+} as a catalyst and H_2O_2 as an oxidant to oxidize organic contaminants in wastewater. This study aims to determine the operating conditions of the Fenton Process with the target characteristics of treated spent caustic meet the WWTP (Waste Water Treatment Plant) inlet specifications and to make the design process of spent caustic treatment with the Fenton Process capacity of 10 m^3/day. By operating at the H_2O_2/Fe (II) ratio of 1.8, the final target was achieved with COD of 810 ppm, ammonia of 22.84 ppm, sulfide of 60.93 ppm and phenol of 14.56 ppm. Total Capital Investment (TCI) for the design is US\$ 2146701.89 whereas Total Manufacturing Cost of US\$ 2089740.75.

Keywords: *spent caustic; refinery wastewater; Fenton process*

INTRODUCTION

In the petroleum refinery, removing contaminant presents in hydrocarbons such as mercaptans and hydrogen sulfide is one of the biggest challenges to get a valuable product. Impurities contained in the hydrocarbons that can cause corrosion are purged by the scrubbing process using a caustic solution, producing a wastewater effluent known as spent caustic (Sabri *et al.*, 2018). Crude oil used in the

primary process of oil refinery highly affects the type of spent caustic viz. sulfidic, naphthenic, and cresylic (Barge and Vaidya, 2018). Sulfidic spent caustic produced from the processing of fuel gas and Liquefied Petroleum Gas (LPG) contains high concentrations of sulfides and mercaptans. Naphthenic spent caustic produced from the processing of diesel and jet fuel contains high concentrations of polycyclic aliphatic organic compounds, for instance, naphthenic
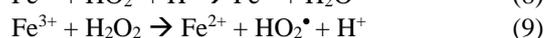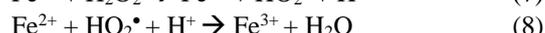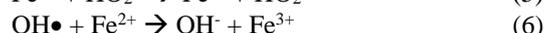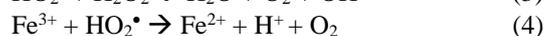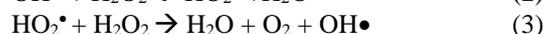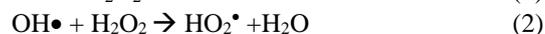
acids, while cresylic spent caustic produced from the processing of gasoline contain high concentrations of organic compounds, including phenol and thiols may also contain sulfide and mercaptans (Seyedin and Hassanzadeganroudsari, 2018a). Oil refinery normally does not split up spent caustic wastewater into the types but mix it which is known as a 'mixed refinery spent caustic'.

Refinery spent caustic contains toxic pollutants such as natrium hydroxide 6-13%wt, phenol, aldehydes, mercaptans, amine, paraffin, thiols and naphthenic emulsion bring unique characteristics such as strong odor, high pH of about 12-14, salinity 5-12%wt and high sulfide levels (1-4%wt) (Ben Hariz *et al.*, 2013; Barge and Vaidya, 2018; Seyedin and Hassanzadeganroudsari, 2018a). Due to the high content of contaminants in the spent caustic, a very high concentration of Chemical Oxygen Demand (COD) becomes a tremendous problem in treating spent caustic to be able to dispose of the environment and not harmful to the aquatic ecosystem and human health. Oxidation technology and biological treatment are common of spent caustic treatment (Baxter *et al.*, 2008). Biological treatment is not up to the task of treating and disposing of spent caustic because high pH, sulfide and COD content in the spent caustic affecting in performance of bacteria as a catalyst in the process so that it inhibits the process of degradation of organic compounds in the biological system, moreover spent caustic contain naphthenic acids which has low biodegradability can have a significant negative impact on the operation as a result of foaming in the aeration basin, effluent toxicity, oil emulsification, and impaired bio flocculation (Oilandgasonline.com, 2018; Seyedin and Hassanzadeganroudsari, 2018a, 2018b). Therefore, oxidation technology is the fundamental of spent caustic treatment so that biological treatment's operational problem could be eliminated. Oxidation technology is used as a pre-treatment followed by biological treatment in the concern of the high-cost requirement for spent caustic treatment and neither effective nor efficient to mineralization completely using oxidation technology.

Advanced Oxidation Process (AOPs) is defined as a process that associates the formation of hydroxyl radical (•OH) to oxidize organic contaminants in wastewater (Barbusiński, 2009; Pawar and Gawande, 2015). AOPs can be used in refinery wastewater treatment to reduce all organic pollutants (COD), degrade the specific pollutants, sludge treatment, improve the organic bioavailability as well as reduce color and strong odors. This process is one or a combination of several processes such as ozone (O_3), hydrogen peroxide (H_2O_2), UV radiation, Titanium Oxide (TiO_2-photocatalyst), Fenton process, as well as some other process that can produce hydroxyl radical. Fenton process is the oxidation of the organic substrates by iron (II) and hydrogen peroxide (called Fenton's reagents). Fenton process uses

hydrogen peroxide as an oxidant and Fe^{2+} as a catalyst (Long, 2007; Barbusiński, 2009; Pawar and Gawande, 2015; Wang *et al.*, 2016). Fenton process applied in various industrial waste, for instance, textile waste, laboratory waste, olive oil waste, pulp and paper mill waste, cosmetic and pharmaceutical waste as well as waste with high phenolic compound content (Long, 2007). The advantages of the Fenton process can oxidize some low molecular weight organic compounds (such as paraffin, chlorinated alkanes, and some short-chain carboxylic acids), high-efficiency process, ease of operation because of operating at room temperature and atmospheric pressure, and a more environmentally friendly waste effluent (Long, 2007). Unfortunately, the Fenton process has several disadvantages such as high operational cost, optimum pH range limitations (optimum operating at pH of 3), high sludge iron volume and the difficulty of the Fe^{2+} catalyst recycle process.

Indonesia's Petroleum Oil Refinery produced the amount of spent caustic wastewater from LPG processing with the characteristic of pH about 12-14 and the range of COD content 5000-30000 ppm. There is a Spent Caustic Treatment (SCT) Unit at this plant but undergo overload routinely due to insufficient capacity. By design, the SCT Unit in a refinery with a capacity of 4.8 m^3/day can reduce COD content to 2000 ppm. While there are 10 m^3/day of spent caustic that cannot be treated by the SCT Unit due to an increase in LPG production. As a result, untreated excess spent caustic was submitted to a third-party for further treatment. However, this raises new problems like the emergence of a strong odor during transportation to the third-party impacting on the environment and inhabitants resulting in no transporter willing to transport the spent caustic waste. It is necessary to conduct a study related to the right spent caustic treatment before being injected into the biological treatment as an effort to prevent pollution to the environment.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \qquad (1)$$
$$OH\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad (2)$$
$$HO_2^\bullet + H_2O_2 \rightarrow H_2O + O_2 + OH\bullet \qquad (3)$$
$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \qquad (4)$$
$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \qquad (5)$$
$$OH\bullet + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad (6)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \qquad (7)$$
$$Fe^{2+} + HO_2^\bullet + H^+ \rightarrow Fe^{3+} + H_2O \qquad (8)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \qquad (9)$$

Although, hydrogen peroxide is a strong oxidant still H_2O_2 alone is not effective for high concentrations of certain refractory contaminants because of low rates of reaction at a reasonable H_2O_2 concentration (Pawar and Gawande, 2015). In the Fenton process, H_2O_2 is activated by metal salts, i.e. iron salts to form OH• radical, which are strong oxidants, that attack and destroy many hazardous

organic pollutants in water. Radical $HO_2^\bullet$ is also formed as active intermediates in the reaction (Barbusiński, 2009; liu, 2018).

The formation of radical OH• is a complex reaction. Reaction (1-3) are a chain initiation phase that consists of a series of single electron transfer reaction between Fe^{2+} and H_2O_2, OH• and H_2O_2, $HO_2^\bullet$ and H_2O_2 and the generated oxygen free radicals induce the chain growth process (OH•, $HO_2^\bullet$) (Barbusiński, 2009; Telles and Granhen Tavares, 2012; liu, 2018). This phase is followed by chain termination in reaction (5-6). Ferric ion produced in reaction (1) further catalyze hydrogen peroxide which decomposes into water and oxygen. Hydroxyl radicals which generated in the reaction above can oxidize organic substrate (RH) of wastewater as shown below

$$RH + OH\bullet \rightarrow H_2O + R\bullet \quad (10)$$
$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \quad (11)$$
$$R\bullet + O_2 \rightarrow ROO\bullet \quad (12)$$

Organic radical (R•) which is highly reactive as produced by the abstraction of protons.

The objectives of this study are to identify the appropriate operating process conditions according to spent caustic type in this refinery to meet biological treatment feed specifications and to create design spent caustic treatment using a Fenton process with a capacity of 10 m^3/day.

MATERIALS AND METHODS
Materials and Reagents

Samples of the spent caustic wastewater were collected in the worst spent caustic. Spent caustic wastewater samples were obtained from an Indonesia's Petroleum Oil Refinery that uses perforated trays for extraction and prewash system in LPG processing. The process is mixing hydrocarbon stream and regenerated caustic (sulfidic caustic) for H_2S removal continued washing the hydrocarbon with the caustic counter-currently for mercaptan extraction. Spent caustic that produced from this process is sent to the vessel for disengaging any entrained LPG in the liquid from the caustic. After the separation steps, spent caustic is transferred to a storage tank. Samples were stored in a chemical plastic container under refrigeration at 4°C until use. The pH of the solution was adjusted to the required value with 98%wt hydrogen sulfide. Indeed, imperious reagents used in this experiment are 35%wt hydrogen peroxide (technical) and $FeSO_4$ as well as NaOH as a pH controller in effluent streams.

Experimental Procedures

The preliminary experiments were carried out to analyze the characteristic of the spent caustic wastewater samples with a parameter of pH, COD, ammonia, sulfide, and phenol content. Following the samples were processed with Fenton Process by the

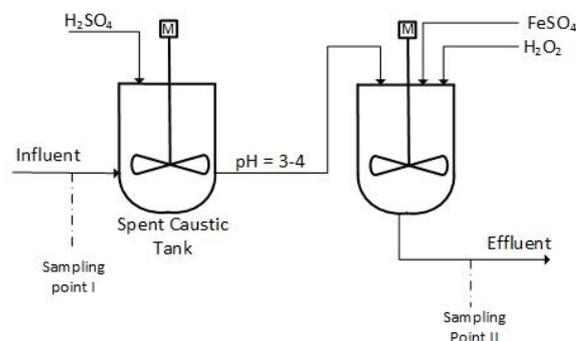duration of an hour at ambient temperature and pressure.

Figure 1. Scheme for Fenton Process Experiments

Prepare 250 mL of bottle Schotts of the spent caustic wastewater to then adjust pH about 3 by adding H_2SO_4 and mixing them in the tank. Next, add the catalyst of $FeSO_4$ and hydrogen peroxide for each variable to the mixing tank (Fig. 1). The effluent was analyzed with a parameter as a preliminary test to obtain the required condition of the biological treatment feed specification.

Analytical

Influent and effluent of the experimental are analyzed for the parameters of pH, COD, ammonia, sulfide, and phenol using Hanna Instruments HI 8424, HI 93754C-25HR, HI 3824, HI 5413, HI 3864 consecutively.

RESULTS AND DISCUSSIONS
Characterization of Refinery Spent Caustic

Mercaptan Oxidation (Merox) is a general process developed for the chemical treatment of petroleum distillates for removal of sulfur present as mercaptans (Merox Extraction) or conversion of mercaptan sulfur to a less objectionable form (Merox Sweetening). Spent caustic composition is highly fluctuating by depends on the specification of feedstock petroleum, caustic soda concentration and temperature of the system. Spent caustic in Indonesia's Petroleum Oil Refinery is produced from 3 units which process LPG and kerosene. The characteristics of Indonesia's Petroleum Oil Refinery spent caustic used in this work are presented in Table 1. It has a pH > 12; average COD of 30394 ppm; average ammonia of 1697 ppm; average sulfide of 2225 ppm; average phenol of 899.6 ppm.

Table 1. Characteristics of the refinery spent caustic used in this study

No	Analysis	MoC	Average Result		
			Unit 1	Unit 2	Unit 3
1	pH	-	12.98	12.37	13.63
2	COD	ppm	27955.63	7209	56016.67
3	Ammonia	ppm	1391.11	376.33	3322.33
4	Sulfide	ppm	1759.33	376.20	4540
5	Phenol	ppm	1560.66	43	1095

In addition to the previously indicated contaminants, the concentration of another component that exists in the spent caustic was also observed. Based on its characteristics, this wastewater is classified as sulfidic spent caustic.

Data Analysis

This study observed the optimum results of each factor in the Fenton process by evaluating COD removal in spent caustic wastewater. Once getting the optimum parameter, it used as a basis for the next experiments to meet the goal of treated spent caustic can comply with biological treatment feed specification by analyzing of COD, phenol, ammonia, and sulfide content.

FeSO₄ Concentration

A catalyst such as Fe^{2+} in the Fenton process is a determining factor in the success of treating spent caustic. At constant H_2O_2 concentration of 30 Liter per m^3 spent caustic, the trendline of COD content in wastewater slightly decreased over the catalyst $FeSO_4$ increased as illustrated in Fig 2 while the graph shows that the COD values fluctuated with the lowest value at $FeSO_4$ dosage of 40 kg. The efficiency of COD removal is 97%. Increasing the catalyst dosage under the acidic conditions at pH of about 3 boost the formation of OH• radical as equation (1) so that we can get the optimum COD removal. The results of this experiment are in accordance with the previous studies conducted by Long Tengrui et al.,(Long, 2007) in which the COD decreases with the increasing amount of Fe^{2+} to the optimum value (800 ppm) and then increased. However, the dosage of $FeSO_4$ must be appropriate considering a raise in production costs as well as the volume of iron sludge. Moreover, the generated OH• would be consumed by the excess catalyst if the catalyst loading in the aqueous solution exceeded the optimum range (Pawar and Gawande, 2015).

H₂O₂ Concentration

As the dominant source in producing OH•, peroxide is the most important factor in determining the success of the Fenton Process. The dosing of peroxide is adjusted to the initial COD. The experiment was conducted with 2 variations of constant $FeSO_4$ concentrations of 10 kg per m^3 spent caustic and 2 kg/m^3, while H_2O_2 concentration is varied from 2 to 10 Liter per m^3 spent caustic. It runs for 5 hours and 2 hours at the first and second variation $FeSO_4$ concentration respectively. Fig 3 illustrates that the COD content of effluent was fluctuated but has a declining trendline both for 2 hours and 5 hours operation. Both variations show that Fenton Process could reduce COD to below 7500 ppm when the dosage of peroxide reached 8-10 Liter per m^3 wastewater.
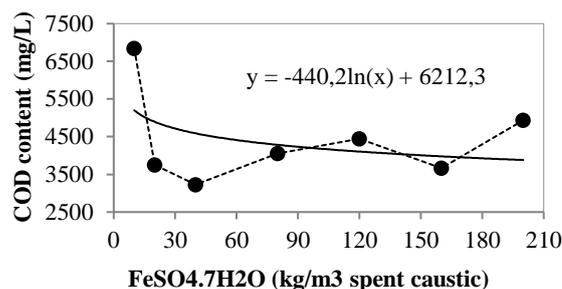
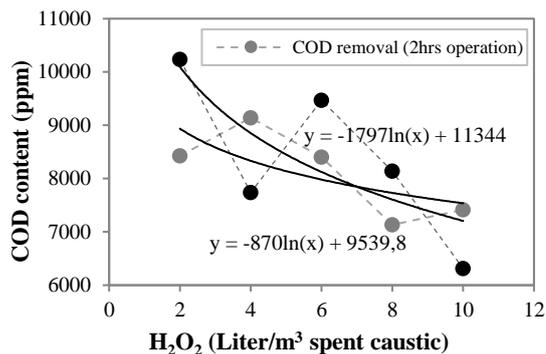Figure 2. The effect of variable $FeSO_4$ on COD content

Figure 3. The effect of variable peroxide on COD content

When the concentration of peroxide is more increased, thus higher hydroxyl radical can be produced then organic can be converted to CO_2 and H_2O more easily. This is in accordance with equation (10). Even though there is a difference of 3 hours for the variation of this experiment, the efficiency of COD removal does not differ much. At the time variable of 5 hours, percent removal of COD up to 94% and 93% of the 2 hours running. The optimum of H_2O_2 concentration is 8 Liter per m^3 then the optimum H_2O_2/Fe^{2+} ratio is 2:1. The ratio in this study is suitable for the prior study conducted by Long Tengrui *et al.* (2007), the H_2O_2/Fe^{2+} ratio is 2.1:1.

Treated Spent Caustic

Based on preliminary experiments with COD analysis at laboratory scale, the variable used in this study per m^3 spent caustic was a pH of about 3, H_2O_2 concentration of 12.5 Liter/m^3, $FeSO_4$ of 10 kg/m^3, and H_2SO_4 of 25 Liter/m^3 applied directly to pilot test in the plant. The concentration of catalyst applied 10 kg/m^3 instead of 40 kg/m^3 as the optimum value because of sludge production concerns. Nevertheless, COD removal when using $FeSO_4$ of 10 kg/m^3 is high enough, 93%. H_2O_2 concentration calculated is 12.5 Liter/m^3 hence we get the final H_2O_2/Fe^{2+} ratio of 1.8 vs 2.0. The experiment was conducted for about an hour. The efficiency of the Fenton Process using these variables is 97%. The effluent has COD content of 810 ppm, ammonia of 46.45 ppm, sulfide of 60.93 ppm and phenol 24.63 ppm. This product specification is received as a feed of biological treatment.
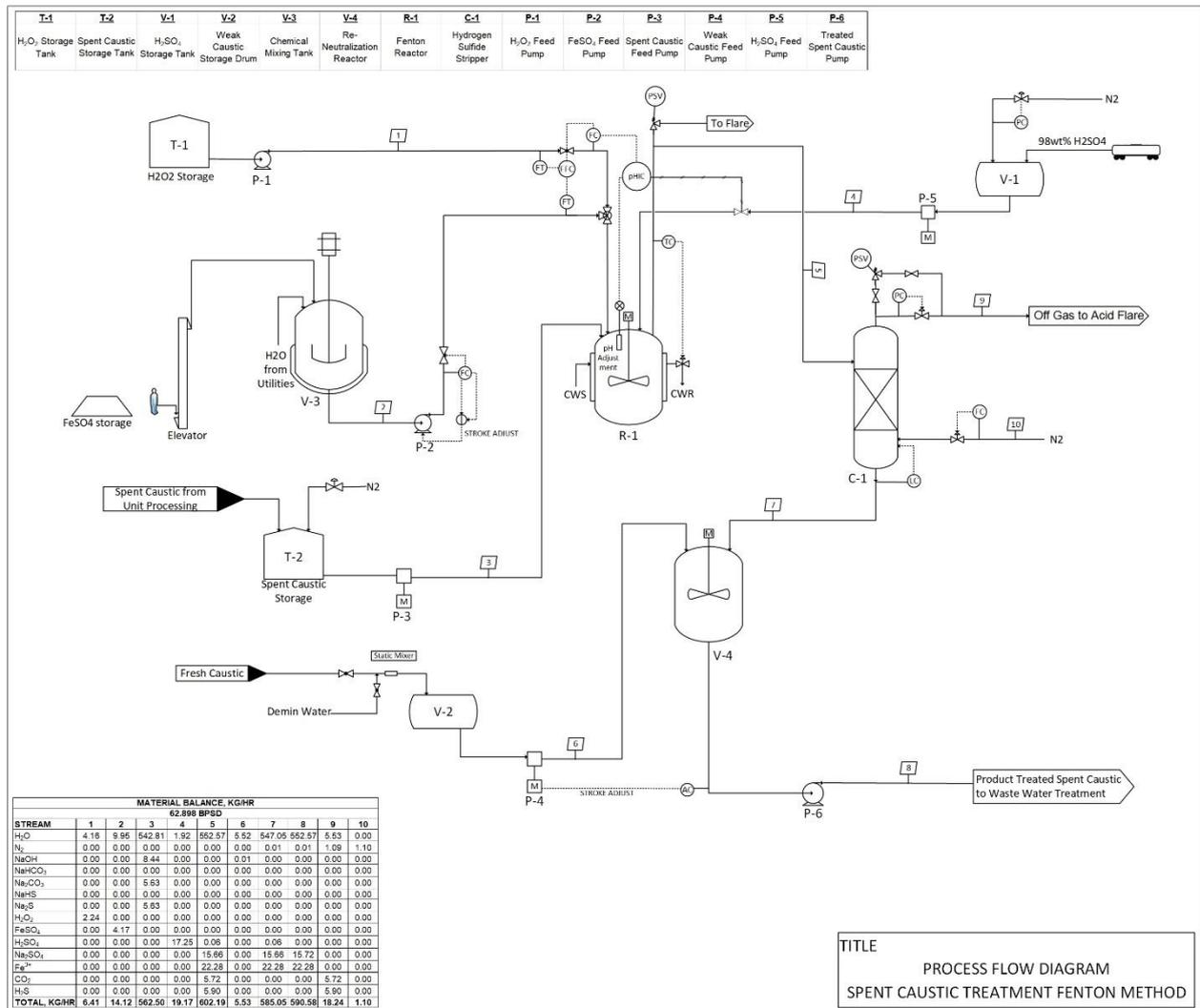
Tag	Name
T-1	H_2O_2 Storage Tank
T-2	Spent Caustic Storage Tank
V-1	H_2SO_4 Storage Tank
V-2	Weak Caustic Storage Drum
V-3	Chemical Mixing Tank
V-4	Re-Neutralization Reactor
R-1	Fenton Reactor
C-1	Hydrogen Sulfide Stripper
P-1	H_2O_2 Feed Pump
P-2	$FeSO_4$ Feed Pump
P-3	Spent Caustic Feed Pump
P-4	Weak Caustic Feed Pump
P-5	H_2SO_4 Feed Pump
P-6	Treated Spent Caustic Pump

MATERIAL BALANCE, KG/HR
62.898 BPSD

STREAM	1	2	3	4	5	6	7	8	9	10
H_2O	4.16	9.95	542.81	1.92	552.57	5.52	547.05	552.57	5.53	0.00
N_2	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	1.09	1.10
NaOH	0.00	0.00	8.44	0.00	0.00	0.00	0.01	0.00	0.00	0.00
$NaHCO_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2CO_3	0.00	0.00	5.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NaHS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2S	0.00	0.00	5.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2O_2	2.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$FeSO_4$	0.00	4.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2SO_4	0.00	0.00	0.00	17.25	0.06	0.00	0.06	0.00	0.00	0.00
Na_2SO_4	0.00	0.00	0.00	0.00	15.66	0.00	15.66	15.72	0.00	0.00
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	22.28	22.28	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	5.72	0.00	0.00	0.00	5.72	0.00
H_2S	0.00	0.00	0.00	0.00	5.90	0.00	5.90	0.00	5.90	0.00
TOTAL, KG/HR	6.41	14.12	562.50	19.17	602.19	5.53	585.05	590.58	18.24	1.10

TITLE

PROCESS FLOW DIAGRAM
SPENT CAUSTIC TREATMENT FENTON METHOD

Figure 4. Process Flow Diagram Spent Caustic Treatment Fenton Method

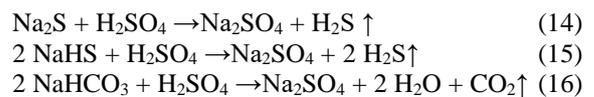### Design Fenton Process Spent Caustic Treatment

Spent caustic from Unit 1, 2, and 3 are routed to the SCT Unit with a capacity of 10 m³/day and stored in Tank-2 (T-2) Spent Caustic Storage. 98 wt% H_2SO_4 solution which used to neutralize spent caustic is loaded from tankers (lorry) and stored in the H_2SO_4 storage drum (V-1). 50.55 wt% H_2O_2 solution is loaded from Intermediate Bulk Containers (IBC) Tank and stored in the H_2O_2 storage tank (T-1) with a capacity of 4.125 m³. Preparations were carried out for solid $FeSO_4.7H_2O$ before being flowed to the batch reactor for treating spent caustic using Fenton Process, which was dissolving in the Mixing Tank (V-3). Spent Caustic, $FeSO_4$ solution and H_2SO_4 flow into the reactor (R-1) up to reach a pH of about 3. Through the pH Indicator Control, it gives a signal to flow H_2O_2 to R-1 according to the H_2O_2/Fe^{2+} ratio of 1.8. The residence time of the reactor is calculated based on the following equation

$$t = -\frac{1}{k} ln \frac{C_A}{C_{A0}} \qquad (13)$$

where C_A is COD content of the exit stream and C_{A0} is COD content of the process influent with k value obtained from previous studies, 0.027 min⁻¹ (Matyszczak, Sędkowska and Kuś, 2020) so that the residence time of reactor is 2.24 hours.

The reactor output product enters the hydrogen sulfide stripper to separate CO_2 and H_2S (see equation (13-15)) from liquid with the help of nitrogen then released into an acid flare. Treated spent caustic is pumped to WWT and adjusted the pH of about 7-8 beforehand.

$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S \uparrow$ (14)
$2\ NaHS + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2S\uparrow$ (15)
$2\ NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O + CO_2\uparrow$ (16)

Economic Analysis

The economic feasibility for this technology is calculated based on 2 components: Capital Investment and Manufacturing Cost. Capital Investment includes Fixed Capital Investment and Working Capital while Manufacturing Costs include Direct Manufacturing

Costs, Indirect Manufacturing Costs, and Fixed Manufacturing Costs.

To consider the change in equipment cost over time, chemical engineering plant cost index (CEPCI) is used for the Fenton process reactor, storage tank, mixing tank, re-neutralization tank and pump to reflect the value of money over time (Equation (17)).

$$C_2 = C_1 \text{ x } \frac{CEPCI_2}{CEPCI_1} \qquad (17)$$

where C_1 is equipment cost in 2019 (Peters, 1991), C_2 is adjusted equipment cost in 2022, $CEPCI_1$ is 702.55 and $CEPCI_2$ is 752.69 (Peters, 1991). The result of the calculation for Equipment Cost is US$ 163430.68.

Fixed Capital Investment takes into account Direct Plant Cost (DPC), Contractor's Fee and Contingency with a total of US$ 1193797.71. All costs related to routine operational and maintenance requirements such as purchase equipment cost, installation, piping, instrumentation, electricity, and utility added by Engineering & Construction cost is included DPC. Total Capital Investment (TCI) for this design is US$ 2146701.89 (detail in Table 2).

Direct manufacturing cost covers some matters such as labor cost, supervise, maintenance, plant supplies, and utilities. While indirect manufacturing cost includes payroll and plant overhead. Depreciation, property tax, and insurance are calculated and classified to Fixed Manufacturing Cost. Then, based on calculation obtained a Total Manufacturing Cost of US$ 2089740.75 (detail in Table 3).

Table 2. Total Capital Investment of Spent Caustic Treatment Plant Design

Component	Cost (US$)
Fixed Capital Investment	1193797.713
Working Capital	685405
Plant Start-Up	88429.46
Interest During Construction	179069.66
TOTAL	**2146701.89**

Table 3. Total Manufacturing Cost of Spent Caustic Treatment Plant Design

Component	Cost (US$)
Direct Manufacturing Cost	1835686.35
Indirect Manufacturing Cost	98860.70
Fixed Manufacturing Cost	155193.70
TOTAL	**2089740.75**

CONCLUSION

Fenton Process is currently the most cost-effective technologies available for the reduction of organic compounds in spent caustic which run well in acidic conditions. The COD removal efficiency is 97% which was affected by Fenton reagent dosage. The optimum H_2O_2/Fe^{2+} ratio was 1.8:1 according to the variation of H_2O_2 and $FeSO_4$ concentration. The calculation of residence time obtained 2.24 hours. The effluent has COD content of 810 ppm, ammonia of 46.45 ppm, sulfide of 60.93 ppm and phenol 24.63 ppm. This product specification is received as a feed of biological treatment. Feasibility study for Spent Caustic Treatment Unit has a total capital investment of US$ 2146701.89.

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