Making of KCl liquid fertilizer from liquid waste manufacture of seaweed and galvanized industry

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Abstract. The seaweed processing industry uses potassium hydroxide (KOH) in the seaweed cooking process, while the galvanized industry uses hydrogen chloride (HCl) in the pickling process. Liquid waste from these two types of industries can cause environmental pollution if not managed properly. This study aims to utilize liquid waste from the seaweed processing industry and galvanized industry into KCl liquid fertilizer as an effort to manage the environment while providing economic value for waste. The quality of liquid waste from the seaweed processing industry, liquid waste from the galvanized industry, KCl liquid fertilizer and the content of heavy metals in fertilizer are analyzed through experimental testing using SNI and AOAC methods. The results showed that liquid waste from the seaweed processing industry can be utilized together with liquid waste from the galvanized industry to produce KCl liquid fertilizer that meets the requirements of SNI 02-2805: 2005 and Minister of Agriculture Regulation Number 43 / Permentan / SR.140 / 8 / 2011. Potassium levels as K2O from KCl liquid fertilizer produced ranged from 727 – 16443 ppm, where the value is higher than the standard according to SNI 02-2805: 2005 of 600 ppm. The content of heavy metals in liquid fertilizer produced meets the requirements of the Minister of Agriculture Regulation No. 43 / Permentan / SR.140 / 8/2011. Consequently the range of heavy metals contained in liquid fertilizer produced by As, Hg, Cd, and Pb is 0.0032 – 0.034 ppm, 0 – 0.0007 ppm, 0.0064 – 0.0546 ppm, and 0.0006 – 0.3497 ppm, where the values of this is lower than the standard according to Regulation of the Minister of Agriculture No. 43 / Permentan / SR.140 / 8/2011 namely As (max 100 ppm), Hg (max 10 ppm), Cd (max 100 ppm), and Pb (max 500 ppm).

1. Introduction

Data from the Central Statistics Agency (BPS) noted the industrial sector is still the largest contributor to the national Gross Domestic Product (GDP) with achievement of 20.16% in 2017. The growth of the non-oil and gas processing industry amounted to 5.14% in the fourth quarter of 2017. The sub-sectors that experienced the highest growth in the fourth quarter of 2017, namely the food and beverage industry by 13.76%, the machinery and equipment industry 9.51%, the base metals industry 7.05%, and the textile and apparel industry 6.39%.

Seaweed is one of the promising fishery communities that have high economic value [1]. One of the growing food and beverage industries in Indonesia is the seaweed processing...
industry. The number of seaweed processing industries operating in Indonesia currently reaches 20 companies spread across several locations such as West Java, Banten, East Java, Central Java, South Sulawesi and West Nusa Tenggara [2]. The current seaweed processing industries in South Sulawesi include PT. Bantimurung Indah in Maros, PT. Giwang Citra Laut in Takalar, PT. Agarindo Bogatama, CV. Cahaya Cemerlang in Makassar, and PT. Wahyu Putra Bimasakti in Makassar.

PT. Wahyu Putra Bima Sakti processed Cottonii seaweed into SRC (semi refined carrageenan) and ATC (alkali-treated cotton) products. From this production activity, wastewater is produced around 8-22 m$^3$/day. The characteristics of seaweed leaching waste produce, among others, COD and high pH [3]. K Adar potassium and chloride seaweed waste grama h greater than of artificial fertilizers around 0.87 to 2.88% [4]. With this very high pH level, the liquid waste of the seaweed processing industry can cause environmental pollution if it is directly discharged into water bodies such as rivers or the sea, so it needs to be treated first [5]. However, this seaweed liquid waste also has high potassium content, so that it has the potential to be used as potassium inorganic fertilizer. Seaweed wastewater treatment can be done at the same time can utilize the element of potassium as an inorganic fertilizer for plants.

The BPS DATA also shows that the base metal industry is also experiencing developments other than the food and beverage industry. One example of a growing metal industry is the galvanized and electrophating industry. The galvanic industry is growing along with the increasing public demand for industrial products made from metal raw materials. Industries made from metal (for example zinc) generally involve a coating process to prevent corrosion [6]. Galvanized industrial products include construction materials, electronic tools, transportation materials, and mild steel for housing.

One of the galvanic industries that produce zinc is PT. S Erman Steel. PT. Sermani Steel is in South Sulawesi, has a production of around 10,000 - 20,000 tons/year (installed engine capacity is 40,000 tons/year). Products produced such as zinc roof Sermani, Sermani spandex, sermani galvalume, and Sermani coil galvalume. In the process of coating steel by zinc, the surface of the steel must be cleaned first through the galvanizing process. To clean the steel surface from impurities used HCl solution. Within a certain time the HCl solution can no longer be used and will become liquid waste. This liquid waste is acidic because it has a pH value of 1-4. If the liquid waste is discharged directly into the environment, without going through proper treatment it will cause pollution.

Liquid waste from the seaweed processing industry that is alkaline can be neutralized by using HCl to obtain KCl fertilizer [7]. Liquid waste originating from PT. Wahyu Bima Sakti contains KOH, while liquid waste from PT. Sermani Steel contains KCl. The reaction that occurs from the mixture is a neutralizing reaction that is the reaction of KOH with HCl and will produce KCl.

Based on the foregoing, have carried out research mixing of liquid industrial waste processing seaweed containing KOH at. Wahyu Putra Bimasakti and galvanized industrial liquid waste containing HCl at PT. Sermani Steel to produce KCl liquid fertilizer with the aim of helping the seaweed industry and galvanized industry in improving the performance of its environmental management while providing added value that can be of economic value.

2. Materials and Methods
2.1. Research location and design
The location of seaweed processing industry liquid waste at PT. Wahyu Putra Bimasakti at Jalan Kima Raya I Number 1, Daya, Biring Kanaya, Makassar City, South Sulawesi 90241, while the galvanized industrial liquid waste was taken from PT. Sermani Steel on Jalan Urip Sumoharjo Km 7 Tello Baru Makassar. Research and testing of the measured parameters will be carried out experimentally at the Makassar BBIHP Test Laboratory located at Jalan Prof. Dr. Abdurrahman Basalamah Number 28, Karampuang, Kec. Makassar, Makassar City, South Sulawesi 90231.

This type of research is an experimental study that aims to reduce the negative impacts arising from industrial liquid waste through processing into KCl liquid fertilizer. Industrial wastewater used in this experiment is liquid waste from the seaweed processing industry and galvanized the industry.
This research was conducted through three stages, namely: (1) Stage of the quality testing process of each wastewater used in the study. (2) The stage of making KCl fertilizer, which is the process of mixing the two types of waste used to get a formulation with neutral pH value. (3) Stage of the quality testing process of KCl liquid fertilizer, including nutrient content and heavy metals.

2.2. Population and sample
The population of this research is liquid waste from the seaweed processing industry at PT. Wahyu Putra Binasakti and liquid waste in the galvanized industry at PT. Sermani Steel. A sampling of liquid waste used in research is done by means of a moment (grab sampling). Samples of wastewater derived from seaweed processing industry taken from several points of the processing, i.e., before the cooking (P0), first washing (P1), second washing (P2), and third washing (P3). For liquid waste samples from the galvanized industry (G) taken from the pickling process. The volume of each sample is 2 liters.

2.3. Data analysis
To find out the content of nutrients and heavy metals contained in the test sample and the resulting liquid fertilizer, the test method is used according to the SNI and AOAC methods, such as in Table 1.

3. Results
3.1. Liquid waste of grass processing industry
Based on Table 2, the pH value in sample P1 has increased compared to sample P0, then this pH value has decreased in samples P2 and P3. Likewise, with the content of P2O5, N, K in sample P1 has increased compared to sample P0, then the content has decreased in samples P2 and P3. The Cl- content in the samples P1, P2, and P3 have decreased compared to the P0 sample.

3.2. Galvanized industrial liquid waste
Liquid waste used in this study came from the pickling process, which is the process of immersing raw materials in HCl liquids. Galvanized industrial liquid waste has a pH of 3.16. Galvanized industrial liquid waste has a chloride content of 74624 ppm. This value exceeds the minimum technical requirements of organic fertilizer from industrial wastewater treatment plants, where the total Cl is a maximum of 5000 ppm.

3.3. Characteristics of KCl liquid fertilizers
In Table 3 the sample volumes of P1, P2, and P3 are determined at 400 mL, while the volume of sample G added to samples P1, P2, and P3 varies depending on the value of each pH. The formulation for PG1 fertilizer requires 75 mL sample G, PG2 fertilizer requires 10 mL sample G, and PG3 fertilizer requires only 3 mL sample G.

In Table 4 there is a decrease in the content of the K2O, KCl and K parameters in the KCl liquid fertilizer produced. The parameter content of K2O in PG1 fertilizer is 5903 mg / L, PG2 fertilizer is 4727 mg / L, PG3 fertilizer is 494 mg / L. The content of KCl parameters in PG1 fertilizer was 9361 mg / L, PG2 fertilizer was 7495 mg / L, and PG3 fertilizer was 784 mg / L. The content of element K in PG1 fertilizer is 4900 mg / L, PG2 is 3924 mg / L, and PG3 is 256 mg / L. Table 5 shows that all samples met the requirements of heavy metal content not to exceed the maximum tolerance limit as inorganic fertilizers.

| Element Type          | Test Method                          |
|-----------------------|--------------------------------------|
| Potassium (K2O)       | SNI 02-2805-1992                     |
| Phosphate (P2O5)      | SNI 2803: 2012 Item 6.3              |
| Nitrogen (N)          | AOAC official method 977.02 19th edition 2012 |
| Zinc (Zn)             | SNI 6989.7.2009                      |
Table 2. Results of seaweed processing liquid waste tests.

| Parameter | Unit | P0  | Q1  | P2  | Q3  | Standard *) |
|-----------|------|-----|-----|-----|-----|-------------|
| pH        | -    | 6.82| 10.32| 9.91| 9.05|             |
| $P_2O_5$  | ppm  | 677.75| 796.75| 608.75| 523.25|             |
| N         | ppm  | 430.10| 568.75| 418.78| 308.43|             |
| $K_2O$    | ppm  | 727 | 16443| 9163| 494| 600 |
| K         | ppm  | 306| 13651| 7607| 411| 523.5 |
| K         | %    | 0.03| 13.65| .76| 0.04| 0.05 |
| Cl-       | %    | 12.09| .21| .22| 0.07| 475.5 |

*) SNI 02-2805: 2005 (1g / 1 liter application)

Table 3. Formulation of Liquid Waste Mixing of Seaweed Processing Industry and Galvanized Industry.

| Industrial Liquid Waste Samples | pH |
|---------------------------------|----|
| Seaweed (pH 10.32) | P1 | 400 mL |
| Galvanized (pH 3.16) | G | 75 mL |
| PG1 | 7.02 |
| Seaweed (pH 9.91) | P2 | 400 mL |
| Galvanized (pH 3.16) | G | 10 mL |
| PG2 | 7.02 |
| Seaweed (pH 9.05) | P3 | 400 mL |
| Galvanized (pH 3.16) | G | 3 mL |
| PG3 | 7.02 |

Table 4. Evaluation of KCl Liquid Fertilizer with SNI.

| Parameter | Unit | PG1  | PG2  | PG3  | Standard *) |
|-----------|------|------|------|------|-------------|
| $K_2O$    | %    | 0.5903| 0.4727| 0.04 29|             |
|           | mg / L | 5903| 4727| 4.29| 600 |
| KCl       | %    | 0.9361| .7495| 0.0784|             |
|           | mg / L | 9361| 7495| 784| 475.5 |
| K         | %    | 0.4900| .3924| 0.0356|             |
|           | mg / L | 4900| 3924| 356| 523.5 |

*) SNI 02-2805: 2005 (1g / 1 liter application)
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Table 5. Heavy metal content of liquid KCl fertilizer.

| Parameter | Unit | PG1   | PG2   | PG3   | Standard *) |
|-----------|------|-------|-------|-------|-------------|
| US        | ppm  | 0.0340| 0.0080| 0.0032| 100 ppm max |
| Hg        | ppm  | 0.0007| 0.0000| 0.0014| 10 ppm max  |
| Cd        | ppm  | 0.0164| 0.0546| 0.0064| 100 ppm max |
| Pb        | ppm  | 0.3497| 0.0006| 0.0130| 500 ppm max |
| Cr        | ppm  | 1.4855| 0.2710| 0.0331|             |

*) Regulation of the Ministry of Agriculture Number 43 / Permentan / SR.140 / 8/2011

4. Discussion

The increase in pH value in sample P1 is caused by the addition of KOH (base) to the cooking process, while the decrease in pH value in samples P2 and P3 caused by the washing process occurs in the dilution process. Seaweed contains chemicals such as potassium, chloride, sodium, magnesium, and sulfur [8]. Grass sea contains nutrients which consist of; N 1.00 %, P₂O₅ 0.05 %, and K 10.00 % [9]. During boiling seaweed is stirred so that heating is evenly distributed [10]. Boiling is intended to increase the carrageenan melting point above the cooking temperature so that it does not dissolve into a paste and to increase the gel strength of the carrageenan [11]. The cooking process will cause the content of P₂O₅ and N contained in seaweed tissue to decompose, resulting in increased content in the P1 sample produced. The content of P₂O₅ and N contained in samples P2 and P3 have decreased due to the staining of the sample in the washing process.

The addition of KOH in the cooking process directly caused the high potassium (K) content in the P1 sample compared to the P0 sample. The potassium (K) content in P2 and P3 samples have decreased due to the sample dyeing in the washing process. In this cooking process the reaction of Cl⁻ with K to KCl causes the content in samples P1, P2 and P3 to be very small compared to samples P0. Waste liquid seaweed processing in these studies has pH of 9.05 to 10.32. Another study reported that the pH value in seaweed wastewater was 9.92-11.76 [4]. The difference in pH values is caused by differences in sampling locations. The threshold value of seaweed processing industries in South Sulawesi is regulated in Governor Regulation Number 69 of 2010 where the standard quality of liquid waste must have a pH of 6-9. Based on this, samples P1, P2 and P3, before being discharged into the environment must be processed first so that it meets the quality standards set by the government. The pH value in the P0 sample of 6.82 is a pH value that is close to neutral. The data shows that the liquid waste before cooking (P0) has the potential to be used as artificial fertilizer, while other liquid wastes (P1, P2, P3) need to be processed further in order to have the pH required for liquid fertilizer which is 4 - 9 according with the regulation of the Minister of Agriculture No. 43 / Permentan / SR.140 / 8/2011. M already whether nutrients can be absorbed by plants is largely determined by soil pH. In general, nutrients are easily absorbed by plant roots at a neutral soil pH and at these pH nutrients are easily dissolved in water.

Nitrogen and phosphorus levels (as P₂O₅) of wastewater are 0.003-0.005% and 0.005-0.008%, respectively. Other studies report phosphorus and nitrogen levels of 0.02 - 0.03% and 0.003 - 0.207% [4]. This difference in value is due to differences in the location of sampling and the analyzed sample. Pre-washing liquid waste samples (P0) contain P₂O₅ and N content of 0.006% and 0.004%, respectively. The P₂O₅ and N content is derived from seaweed raw materials respectively 0.005% and 1% [9]. The content of P₂O₅ and N in this study has the same pattern for each processing point of seaweed where the highest content is in P1, then P0, P2, and P3.

Waste seaweed liquid processing has potassium levels the 0.05 - 1.64% and chloride from 0.07 to 1.21%. H acyl another study reported this is smaller than potassium chloride respectively by 0.87 to 2.88% and 1.37 to 2.41% [3]. Potassium content in seaweed processing wastewater (P0 - P3) is still quite high at 727 - 16443 ppm. The high content of potassium is derived from raw materials and the remaining addition of KOH in the reaction of seaweed farming [12]. Potassium content as K₂O based on SNI 02-2805: 2005 is 600 ppm. So that the seaweed processing wastewater that has the potential to be further processed into liquid fertilizer is P0, P1, and P2. The formulation of making liquid KCl
fertilizer in this study depends on the pH of the liquid waste of the seaweed processing industry. The higher the pH of the seaweed processing industry wastewater, the more galvanized industrial liquid waste is added.

The parameters of the K$_2$O, KCl and K parameters that exceed the SNI value are the PG1 and PG2 products. This is linear with samples P1 and P2 that has the potential to be used as fertilizer. So that the liquid waste of the seaweed processing industry reacted with galvanized industrial liquid waste that meets the SNI requirements is the PG1 and PG2 products. PG3 products do not meet SNI in the parameters K and K$_2$O. Liquid waste of seaweed processing industry can be utilized together with galvanized industrial liquid waste into artificial fertilizer that meets SNI 02-2805: 2005 regarding KCl fertilizer. The test results also showed that all samples fulfilling the requirements of heavy metal content did not exceed the maximum tolerance limit as inorganic fertilizers in accordance with the requirements of the Minister of Agriculture Regulation No. 43 / Permentan / SR.140 /8/2011.

5. Conclusions and suggestions

Liquid waste from the seaweed processing industry can be utilized together with galvanized industrial liquid waste to be made into an artificial liquid fertilizer that can meet SNI 02-2805: 2005 regarding KCl fertilizer. Potassium content as K$_2$O from seaweed processing industrial wastewater that meets SNI 02-2805: 2005 (600 ppm) standards is 727 - 16443 ppm. The process of making KCl liquid fertilizer is by mixing the liquid waste of the seaweed processing industry and the galvanized industrial liquid waste to obtain a neutral pH. The formulation for making liquid KCl fertilizer depends on the pH of the liquid waste of the seaweed processing industry. The higher the pH of the seaweed processing industry wastewater, the more galvanized industrial liquid waste is added. KCl liquid fertilizer from mixing liquid waste that meets SNI 02-2805: 2005 comes from the first washing (PG1) and the second washing (PG2) with K$_2$O content of 4727 - 5903 ppm. In addition to meeting SNI, the content of heavy metals contained in KCl liquid fertilizer produced meets the requirements of Minister of Agriculture Regulation No. 43 / Permentan / SR.140 /8/2011. Further research needs to be done on the potential of liquid fertilizer that utilizes this industrial liquid waste, including the impact of fertilizer use on the environment and the effect of fertilizer on plants and soil.

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