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# Adsorption of Heavy Metal Cr (VI) Using Bio-Sorbent of Tea Dregs: Experimental and Modeling

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## Abstract

Tea plants have been generally known by most of Indonesian as a refreshing drink. Tea leaves usually contain caffeine of 1-4%, tannins of 7-20% and a little essential oil. Powder of tea dregs has the ability to absorb heavy metal of chromium. The research objective was to study the adsorption kinetics of heavy metal ions of Cr (VI) using powder of tea dregs and to study factors that affect adsorption process of chromium metal. The analysis of sample solution concentration of Cr (VI) in this study was using Atomic Absorption Spectrophotometer (AAS). The effect of various process variables such as initial concentration of the metal solution, stirrer speed and concentration of modifying agent of sulphuric acid has been investigated. The results showed that the optimum adsorption process was obtained at adsorbate concentration of 125 ppm with activation process at sulphuric acid concentration of 0.8 M. The highest efficiency of heavy metal adsorption reached 83.24% with adsorption capacity of 5.202925 mg/g bio-sorbent. This adsorption was in accordance with the Langmuir Isotherm models with R<sup>2</sup> value of 0.909. This study was also in accordance with kinetics of a second pseudo order with a R<sup>2</sup> value of 0.997 and K of 0.752 g/mg. Minute.

Key words: powder of tea dregs, bio-sorbent, heavy metals, bio-sorption

## Introduction

Chromium is one of high toxicity metals that pollute our environment. Chromium toxicity depends on its ion valence. Cr<sup>6+</sup> ion is the most widely studied Cr form because Cr<sup>6+</sup> is highly toxic, corrosive and carcinogenic. Cr<sup>6+</sup> can form complex macromolecules in cells, in addition to the chemical structure can penetrate cell membranes rapidly and undergo a reaction in the cell. The level of chromium poisoning in humans is measured through the content of chromium in the urine. The penetration of chromium into the human body through food and drink can eventually accumulate in the liver and kidneys simultaneously and for a long time will precipitate and can cause cancer (Danarto, 2007).

Nowadays, research with topics of alternative adsorbents derived from nature (biosorbent) which has a good adsorption ability, low cost and environmentally friendly adsorbent were studied by many researchers (Mariana et al, 2012). Jalali et al (2002) used seaweed adsorbents to take the metals of Pb, Chandrasekhar et al (2002) used Garcinia Cambogia fruit as an adsorbent for uptaking Cr, Adhiya et al (2002) used *Chlamydomonas reinhardtii* typed bacteria to take Cd metal. The use of activated carbon has also been studied as an alternative adsorbent and Juang et al (2002) used activated carbon adsorbents derived from sugar mill waste (bagasse). While Abriagni (2011) used the dregs of tea leaves (*Camellia sinensis*) as an adsorbent for adsorption optimization of chrome. Abriagni (2011) indicated that waste tea leaves can absorb the waste of Cr(VI) as much as 0.334775 mg from the initial mass of 0.562945 mg and the percentage of adsorption is 59.46%. The adsorption is

still below 60%. Therefore it is necessary to do further research on the use of powder of tea dregs as biosorbent for the absorption of Cr(VI) from wastewater. This study used powder of tea dregs as biosorbent for uptaking chromium metal from liquid waste, fundamental differences of this study with research Abriagni (2011) is biosorbent physical properties. Abriagni (2011) used waste from the manufacturing plant of tea while this research used of waste dregs of tea that is used in everyday life. Tannins contained in tea that causes the tea to absorb heavy metals. It is known that the presence of the carbonyl bond in tannins makes it easy protonated molecule or negatively charged so that easily to absorb cations. Tannin content presented in tea around 20%.

The purpose of this research is to understand the mechanisms of heavy metal adsorption using bioadsorbent tea waste and heavy metal absorption capability by bioadsorbent that has been added by modifying agent which serves to remove dissolved organic compounds so that can improve the efficiency of absorption

## Research Methods

### Equipmentss and materials

The main equipments used in this study are Atomic Absorption Spectrophotometer (Shimadzu AA-6300), Instrumentation Tester Surface morphology (Scanning Electron Microscopy), FTIR (Fourier Transformed Infrared Spectroscopy), pH Meter, analytical scales, magnetic stirrer and oven dryer. Materials used included powder of tea dregs,  $K_2Cr_2O_7$ ,  $H_2SO_4$ , distilled water, filter paper and aluminum foil.

### Modification Process of Tea Dregs Bioadsorben

In this study biosorbent used is powder of tea dregs obtained from the tea dregs that has been used in everyday life. Firstly, the tea dregs were washed using distilled water to remove the dye and dirt, then activated by using a modifying agent of  $H_2SO_4$  at different concentrations for 60 minutes. After activating and filtering process, the adsorbent was washed by using distilled water until a pH around 7, and finally was dried for 24 hours at a temperature of 105 °C in oven dryer.

### The Adsorption Process of Heavy Metal Ion by Activated Bioadsorbent

At this stage, activated biosorbent was contacted with various concentrations of  $K_2Cr_2O_7$  solution for 60 minutes at two different stirrer speeds of 80 and 100 rpm at room temperature. After adsorption process finished, the solution was separated by using a filter paper, then the cake (biosorbent) was analyzed its morphology by SEM, while the filtrate was analyzed for final chromium concentration by using AAS to determine the percent of Cr (VI) uptaking.

## Results and Discussion

### Surface Characterization of Powder of Tea Dregs Biosorbent

Biosorbent characterization process of structure morphology was done by analyzing biosorbent before and after the adsorption process using analytical tools Scanning Electron Microscope (SEM) as shown below.

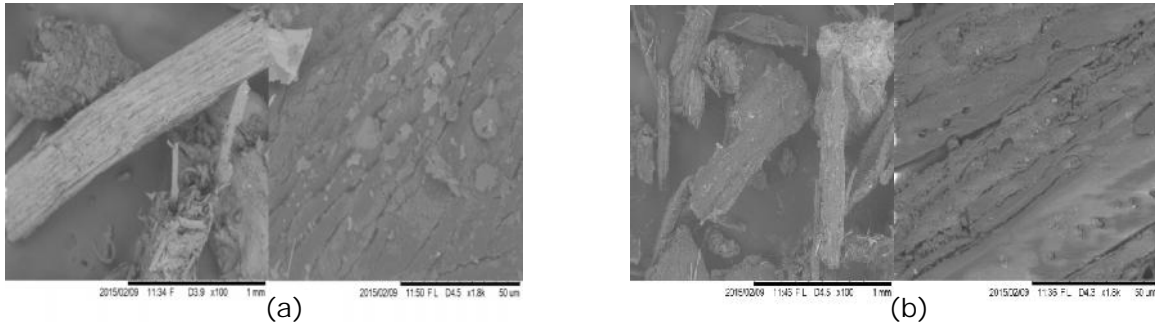


Figure 1. Morphology and size pore of biosorbent (100x and 1800x magnification): (a) without activation with  $H_2SO_4$ ; (b) After activation with  $H_2SO_4$

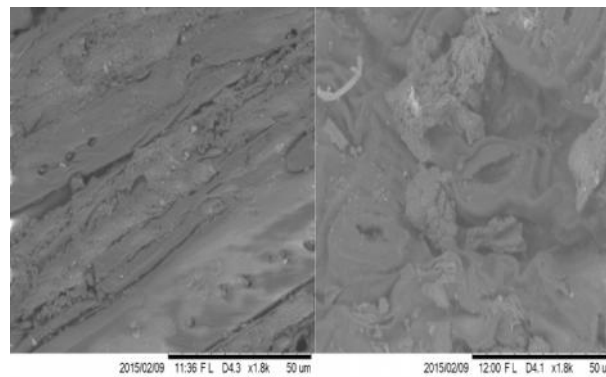


Figure 2. Morphology of activated biosorbent before adsorption process of Cr (VI) and after adsorption process of the Cr (VI)

Figure 1a is powder of tea dregs without activation where the figure showed that the pore surface of biosorbent was still very small, whereas in Figure 1b of powder of tea dregs after activation showed that the pores on the surface of biosorbent seem obviously, it is proved that the activation aims to open up the pores on biosorbent surface was achieved. Figure 2 showed the difference between the surface morphology of biosorbent before and after contacting with  $K_2Cr_2O_7$  solution. At sample of biosorbent before contacting with adsorbate it was viewed that the surface of adsorbent was a lot and in order shape. However, the image of biosorbent after contacting with adsorbate showed that the pores became less and surface of pore slightly wider due to absorption of Cr (VI) inside. Without activation obtained the pore size around  $8,096 \mu m$  ( $80,960 \text{ \AA}$ ), whereas the activation obtained the pore size of  $22,185 \mu m$  ( $221,850 \text{ \AA}$ ). Secondary data obtained that the pore size of Cr(VI) is  $48 \text{ \AA}$ . This indicates that the pore of tea dregs possible to absorb Cr(VI).

#### Effect of Activation Concentration of Biosorbent against Adsorption Capacity and Adsorption Efficiency

Suarya (2008) suggested that activation of the adsorbent using the acid will produce the adsorbent with larger active sites and larger surface acidity, so that it will produce the adsorbent with higher adsorption capacity than before activation. The success of the adsorption process with various concentrations of biosorbent can be proved from the results of the analysis using the tool AAS (Atomic Adsorption Spectrophotometer).

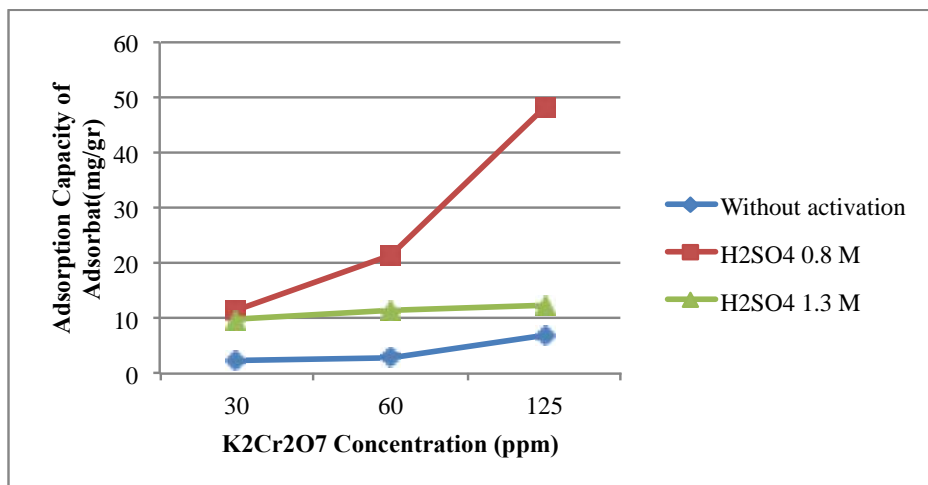


Figure 3. The relationship between the sulphuric acid concentration (M) and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> concentration (ppm) toward adsorption capacity of the adsorbate at a stirrer speed of 80 rpm

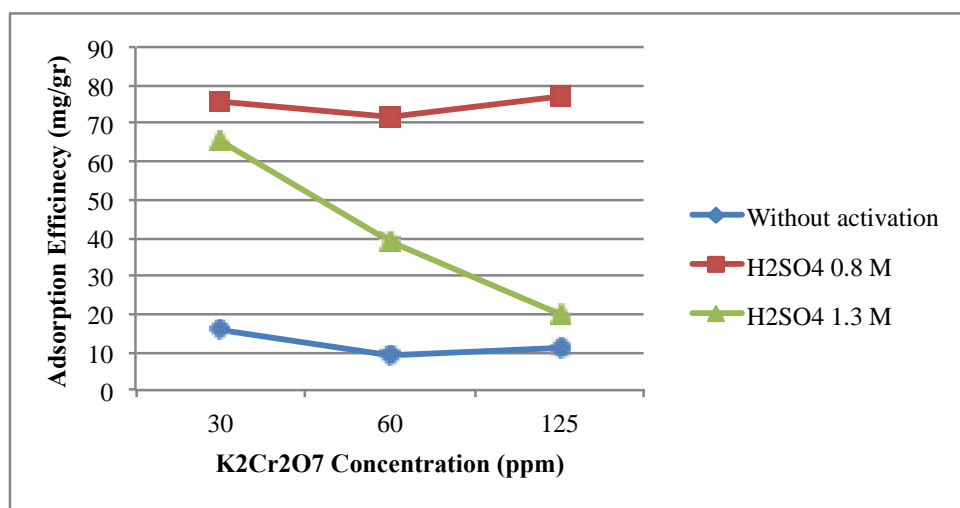


Figure 4. The relationship between the sulphuric acid concentration (M) and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> concentration (ppm) toward the adsorption efficiency at a stirrer speed of 80 rpm

Figures 3 and 4 showed the ratio of adsorption between biosorbent with activation and without activation. A best adsorption capacity occurred if biosorbent was treated by using H<sub>2</sub>SO<sub>4</sub> which aims to increase the surface area of biosorbent. The figure above also showed that surface area of biosorbent decreases with the increase in the concentration of H<sub>2</sub>SO<sub>4</sub>, wherein activation of 1.3 M H<sub>2</sub>SO<sub>4</sub> would decrease surface area. This phenomenon shows that increasing the modifying agent concentration (H<sub>2</sub>SO<sub>4</sub>) would decrease also the amount of adsorbate that would be adsorbed into adsorbent. According to Hundal et al. (2001) the increasing of modifying agent concentration would not ineffectively form of active sites anymore because of damaging of adsorbent structure. However, in our research, a good adsorption capacity was observed at concentrations of 0.8 M H<sub>2</sub>SO<sub>4</sub> because its adsorbent has a large surface area. This is certainly influenced by the appropriate amount of sulphuric acid concentration during activation process of tea dregs. The low concentrations of sulphuric acid lead to incomplete formation of the active site, on the other hand, the too high concentrations of sulphuric acid will cause damage to biosorbent structure.

### Isoterm Adsorpsi

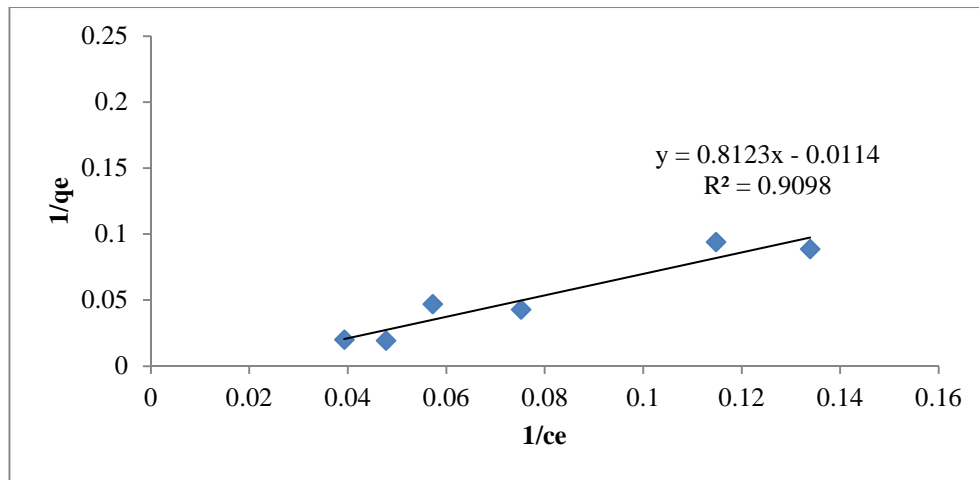


Figure 5. Langmuir isotherm curve on adsorption of Cr (VI) metal ion by H<sub>2</sub>SO<sub>4</sub> 0.8 M activated biosorbent at a stirrer speed of 100 rpm

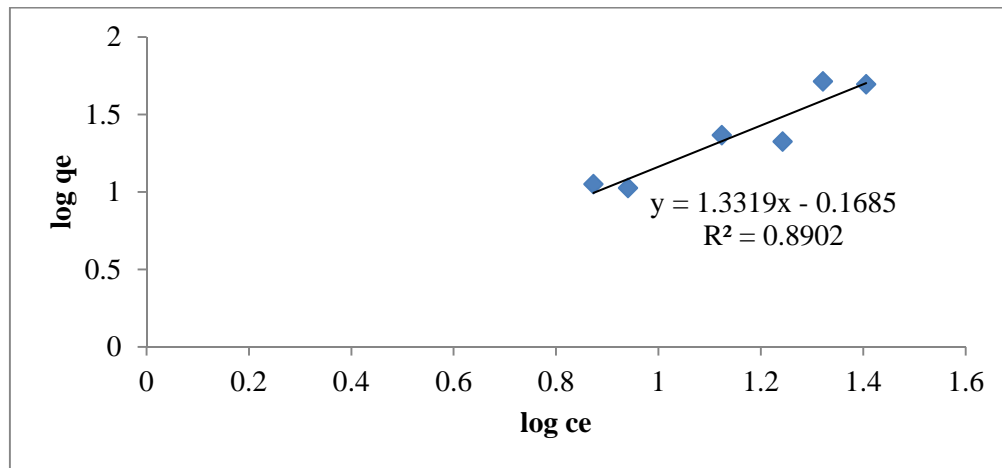


Figure 6. Freundlich isotherm curve on adsorption of Cr (VI) metal ion by H<sub>2</sub>SO<sub>4</sub> 0.8 M activated biosorbent at a stirrer speed of 100 rpm

From Figures 5 and 6 we understand that the correlation coefficient value (R<sup>2</sup>) of Langmuir models was 0.909 and the correlation coefficient value (R<sup>2</sup>) of Freundlich model was 0.890. Based on these two models it was predicted that the adsorption of Cr (VI) using biosorbent of powdered tea dregs followed the Langmuir isotherm models where the value of correlation (R<sup>2</sup>) in Langmuir models are closer to 1 (one).

### Adsorption Kinetics

Figure 7 shows the kinetics rate of first-order where the obtained k value was 0.038 g.mg/min and the obtained q<sub>e</sub> values was -2.57732 mg/g. Figure 8 shows the kinetics rate of two pseudo-order where the obtained k value was 0.752 g / mg.min and the obtained q<sub>e</sub> value was 1.303781 mg/g, so it can be concluded that the process of adsorption of the metal ions Cr (VI) using powdered tea dregs followed the pseudo second order with k values of 0.752 g/mg.min and q<sub>e</sub> value of 1.303781 mg/g with R<sup>2</sup> values of 0.997.

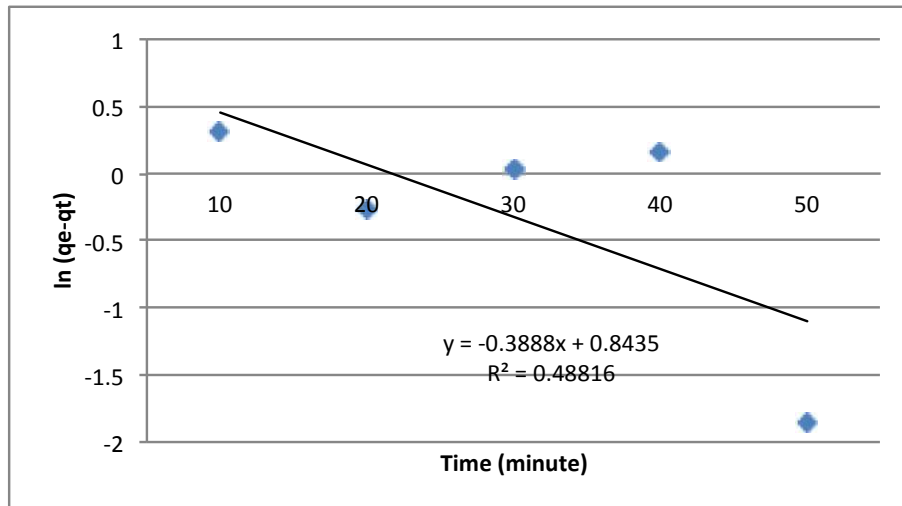


Figure 7. The first-order adsorption kinetics of Cr (VI) adsorption process using biosorbent that was activated by 1 M H<sub>2</sub>SO<sub>4</sub> at adsorbate concentration (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) of 60 ppm and a stirrer speed of 100 rpm

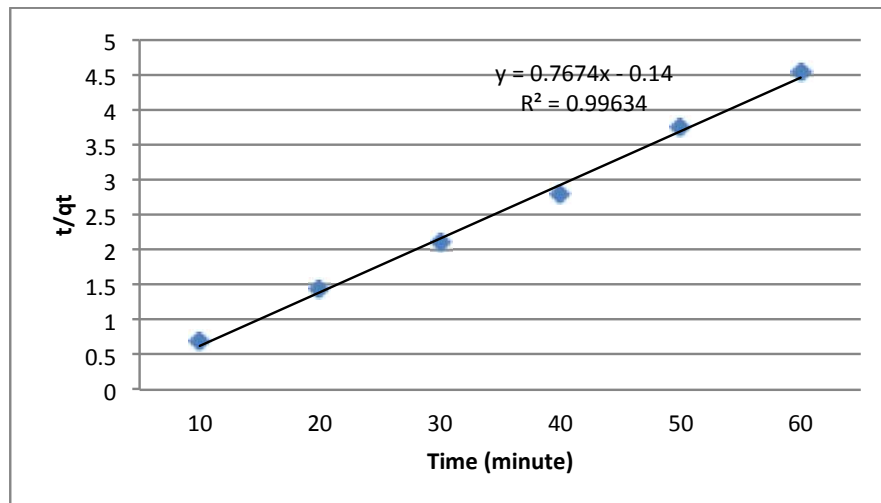


Figure 8. The second pseudo order adsorption kinetics of Cr (VI) adsorption process using biosorbent that was activated by 1 M H<sub>2</sub>SO<sub>4</sub> at adsorbate concentration (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) of 60 ppm and a stirrer speed of 100 rpm

## Conclusions

The highest adsorption efficiency of Cr (VI) metal ion of 83.24% was obtained on adsorbate concentration (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) of 125 ppm by using biosorbent that was activated by 0.8 M sulphuric acid concentration at a stirrer speed of 100 rpm. Adsorption process of Cr (VI) metal ion using powdered tea dregs tends to follow the Langmuir isotherm model with R<sup>2</sup> values of 0.909. Adsorption kinetics in adsorption process of Cr (VI) metal ion by using activated powder of tea dregs follows two pseudo-order kinetics, with k value of 0.752 g/mg.min, q<sub>e</sub> value of 1.303781 mg/g and linear regression value of 0.997.

## References

Abriagni, D. (2011). Optimasi Adsorpsi Krom (VI) dengan Ampas Daun Teh (*Camellia sinensis* L) Menggunakan Metode Spektrofotometri. Thesis. Universitas Negeri Semarang, Semarang.

- Adhiya, J., Chai, X., Sayre, R.T., and Traina, S.J. (2002). Binding of Aqueous Cadmium by the Lyophilized Biomass of *Chlamydomonas reinhardtii*, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 210: 1-11.
- Chandrasekhar, K., Chary, N.S., Kamala, C.T., Supriya, K.R., and Rao, T.R. (2002). Application of *Garcinia cambogia*, A Plant Biomass for Chromium Removal and Speciation Studies, *The International Journal of Environmental Studies*, 5: 1-9
- Danarto, Y.C. (2007). Kinetika Adsorpsi logam berat Cr(VI) dengan Adsorben Pasir yang Dilapisi Besi Oksida, *Ekuilibrium* 6, 2: 65-70
- Hundal, L. S., Thomson, M. L., Laird, D. A., and Carmo, A. M. (200). Sorption of Phenanthrene by Reference Smectites, *Environ. Sci. Technol.*, 35: 3456–3461.
- Jalali, R., Ghafourian, H., Davarpanah, S.J., and Sepehr, S. (2002). Removal and Recovery of Lead Using Nonliving Biomass of Marine Algae, *Journal of Hazardous Material*, B92: 253-262.
- Juang, R.S., Wu, F.C., and Tseng, R.L. (2002). Characterization and Use of Activated Carbon from Bagasse for Liquid-phase Adsorption, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 201, 191-199
- Mariana (2012). Pengaruh Konsentrasi Adsorbat Terhadap Pemisahan Cr (VI) dalam Limbah Cair Menggunakan Daun Jambu Biji, *Proseeding Seminar Nasional Hasil Riset dan Standardisasi Industri II*, Banda Aceh, Indonesia, ISBN: 2302 – 9617.