Biocomposites from anaerobically digested *Eichhornia crassipes* ((Mart.) Solms), as an alternative solution for the post-phytoremediation process

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**ABSTRACT**

Water hyacinth (*Eichhornia crassipes*) is a plant species commonly used for phytoremediation to reduce high chromium content in tannery liquid waste in Garut, West Java. Water hyacinth materials harvested from the phytoremediation can be used for the anaerobic digestion process to produce biogas and bio-slurry. This study aimed to determine the reduction of chromium content found in water hyacinths due to the anaerobic digestion process, and utilization of bio-slurry from the anaerobic digestion process as a biocomposite material. The anaerobic digestion process was carried out for 33 d using biodigesters and the composition of the biodigesters were varied into 100% dried water hyacinths and 80% water hyacinths with the addition of 20% cow dung. The bio-slurry from the anaerobic digestion process was then used for making biocomposites with 3 different compositions, i.e., 75 and 25%; 50 and 50%; and 25 and 75% of cement and bio-slurry, respectively. The average chromium content found in water hyacinths from the phytoremediation process without anaerobic digestion process was 41.964 mg/l. The results show a reduction in the amount of chromium after the anaerobic digestion process was found in each composition of bio-slurry, which were 15.979 mg/l (100% water hyacinth) and 14.861 mg/l (80% water hyacinth + 20% cow dung). Biodigester with a composition of 80% water hyacinth + 20% cow dung produced the highest average volume of biogas which was 0.424 L. The biocomposite of 75% cement and 25% bio-slurry had the highest compressive strength value of 30.598 MPa and water absorption capacity of 37.25%. It can be concluded that biocomposite with the composition of 75% cement and 25% water hyacinth bio-slurry is promising to be used as an alternative material for buildings.

**Keywords:** Tannery waste chromium anaerobic digestion biocomposite

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**1. Introduction**

The leather tanning industry is an economic activity that processes raw materials, semi-finished or finished goods for the manufacture of leather goods as stated by Perda DIY (2016). One of the most important leather-producing areas in Indonesia is Sukaregang village in Garut, West Java. The leather tanning industry produces liquid waste which contains dissolved chemical substances from the tanning process (Paul et al., 2013). Chromium is a chemical tanning agent and about 85% of the world's skin is tanned using chromium (Racordit et al., 2014). Therefore, the leather tanning process produces wastes that contain chromium, a substance classified as a harmful heavy metal (Giacinta et al., 2013).

Chromium from the leather tanning process is generally in the form of trivalent chromium. However, hexavalent chromium is always present in wastewater from the leather tanning process (Giacinta et al., 2013). Heavy metals in liquid waste produced by the leather tanning process may harm human health and the environment because they have toxic properties (Wu and Chen, 2014). A high chromium level of 9.153 mg/l was found in the effluent from the WWTP drains adjacent to the tannery industrial area in Sukaregang, Garut (Taufikurahman et al., 2019). This indicates that the chromium content in water bodies in the Sukaregang area has exceeded the upper limit of permitted chromium content in the waste quality standard according to the Regulation of the Ministry of Environment, which is 0.6 mg/l.

According to Chaney et al. (1995), phytoremediation is the removal of pollutants mediated by plants, including trees, grasses, and aquatic plants. The removal process of pollutants can also be interpreted as the destruction, inactivation, or immobilization of pollutants into harmless forms. According to Upit et al. (2011), water hyacinth was able to reduce the chromium level in batik wastewater by as much as 49.560% after 24 hours of phytoremediation. Water hyacinth is common to be used for animal feed, fertilizer, etc. (Su et al., 2018). However, water hyacinth obtained from the phytoremediation program may contain harmful heavy metals so that further processing is required. Water hyacinth resulted from phytoremediation processes has the potential to be processed into bioproducts in the form of biogas and bio-slurry through an anaerobic digestion method. Anaerobic digestion is a natural process in which organic matter is degraded under oxygen-free conditions into methane (60-70%), carbon dioxide (30-40%), water vapor, nitrogen, hydrogen sulfide, and ammonia by microorganisms (Berglund and Borjesson, 2006).

Bio-slurry resulted from the anaerobic digestion process can be reused to create biocomposites, which can be used as an alternative basic building material or building complementary materials, for example, ventilation blocks (Tsai, 2010). Biocomposite is a combination of two different materials (one of which is natural), in
which one material acts as a matrix/filler and the other acts as a binder (Rudin and Choi, 2012). Meanwhile, a ventilation block can be defined as a building material made from a mixture of cement, fine aggregate, water, and other added materials with various shapes and mounted on walls. Also, ventilation block materials are not only consisted of sand and cement but many other variations could be tested as well, based on their economical factor, convenience factor, etc. This research was carried out with the main objective of utilizing phytoremediation water hyacinth to produce biogas through an anaerobic digestion process and utilizing solid bio-slurry from an anaerobic digestion process to make biocomposites.

2. Materials and methods

2.1. Materials

The experiment was carried out using a completely randomized design with two factors. The first factor was the composition of biodigesters, which are 100% dry water hyacinth and 80% water hyacinth + 20% cow dung with two repetitions for each variation. Biodigester compositions can be seen in Table 1 below. Second factor was the composition of biocomposite which are 75% cement + 25% bio-slurry; 50% cement + 50% bio-slurry; and 25% cement + 75% bio-slurry with three repetitions for each variation. The composition of the biocomposite can be seen in Table 2.

Table 1. Biodigester composition for anaerobic digestion

<table>
<thead>
<tr>
<th>Biodigester</th>
<th>Dried water hyacinth, kg</th>
<th>Cow dung, kg</th>
<th>Water, l</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% WH</td>
<td>0.500</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>80% WH + 20% CD</td>
<td>0.400</td>
<td>0.100</td>
<td>5</td>
</tr>
</tbody>
</table>

2.2. Anaerobic digestion

Anaerobic digestion in this study was carried out using a batch system (Yonathan et al., 2012). The biodigester was made from a used mineral water and a 900 cm³ plastic bag as the gas container connected by a small tube with a diameter of approximately 1 cm. The reaction of biogas formation occurred for 33 d in the biodigester. The biodigesters were placed inside a screenhouse to protect the anaerobic process from drastic changes in environmental temperature or humidity that could be caused by climate change.

2.3. Analysis of the chromium content of water hyacinth from phytoremediation and bio-slurry after anaerobic digestion

The reaction of biogas formation occurred at the rate of 1.313 g/d in the biodigester. The biodigesters were made from a mixture of water hyacinth and cow dung with two repetitions for each variation. The biodigester composition can be seen in Table 1 below. Second factor was the composition of biocomposite which are 75% cement + 25% bio-slurry; 50% cement + 50% bio-slurry; and 25% cement + 75% bio-slurry with three repetitions for each variation. The composition of the biocomposite can be seen in Table 2.

Table 2. Variations of biocomposite composition

<table>
<thead>
<tr>
<th>Code</th>
<th>Bio-slurry, g</th>
<th>Portland Cement, g</th>
<th>Water, ml</th>
<th>Ratio of Cement:Bio-slurry</th>
<th>Ratio of Water:(Cement + Bio-slurry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100C/0B</td>
<td>-</td>
<td>250</td>
<td>85</td>
<td>100% : 0%</td>
<td>0.340</td>
</tr>
<tr>
<td>75C/25B</td>
<td>62.500</td>
<td>187.500</td>
<td>109.375</td>
<td>75% : 25%</td>
<td>0.4375</td>
</tr>
<tr>
<td>50C/50B</td>
<td>125</td>
<td>125</td>
<td>218.750</td>
<td>50% : 50%</td>
<td>0.875</td>
</tr>
<tr>
<td>25C/75B</td>
<td>187.500</td>
<td>62.500</td>
<td>328.125</td>
<td>25% : 75%</td>
<td>1.313</td>
</tr>
</tbody>
</table>

2.4. Analysis of lignocellulose content of water hyacinth from phytoremediation and bio-slurry after anaerobic digestion

Water hyacinth plant and bio-slurry were dried until a constant mass was achieved. The dried water hyacinth was then crushed to produce a fine powder. The powder then was digested using concentrated nitric acid (HNO₃) and acid peroxide (H₂O₂) repeatedly. After the sample has become clear or the green color has gradually disappeared, then the sample was measured using AAS (Atomic Absorption Spectrometry) with a wavelength of 357.9 nm (Putri et al., 2014).

2.5. Biogas measurement

Biogas production was observed by measuring the increasing volume of biogas bag (Ardinal et al., 2015). Using the assumption that the biogas bag has a perfect shape as a tube with an oval-shaped base, the volume of biogas can be calculated using the equation to find the volume of the tube. The following is the equation to calculate the volume of biogas formed in the bag:

\[ Volume = \pi \times \frac{A}{2} \times \frac{B}{2} \times t \]

where A represents the increase in pocket thickness and B represents the coded width of 12 cm. While t is the length of the biogas bag.

2.6. Production of biocomposite

First, the bio-slurry was crushed using a blender and sieved with a micron mesh to produce a fine powder with uniform grain size. The bio-slurry powder and cement were stirred until the mixture was completely homogeneous. After homogenous, the amount of water was added to each mixture. The mixture was stirred again and then poured into the mortar mold. Since this study was a laboratory scale, the size of the biocomposite was reduced into a mortar size for the compressive strength test of 50 mm x 50 mm x 50 mm. Then the biocomposite in the mortar mold was dried for ±14 d.

2.7. Biocomposite compressive strength test

Biocomposite compressive strength testing was carried out for variation codes 100C/0B, 75C/25B, 50C/50B, and 25C/75B with three repetitions for each of these variations, as can be seen in Table 2. Twelve (12) biocomposites were tested for their compressive strength using the Universal Testing Machine.
2.8. Biocomposite water absorption test

The biocomposites that have been printed and dried were then immersed in clean water. According to mortar manufacturing standards, water immersion should be carried out for 28 d. However, due to the high porosity of the sample only 24 hours of immersion of the biocomposite in water was carried out. After 24 hours, the biocomposite was placed on a 45° incline for 10 minutes, then the biocomposite was weighed. Then the biocomposites were dried in an oven at 103 ± 2 °C until their mass was constant (Fig. 1). After constant, the water absorption capacity of the biocomposites was calculated using the equation below.

\[
\text{Water absorption} = \frac{A - B}{B} \times 100\%
\]

Where variable A shows the saturated mass of the biocomposite after soaking (grams), while variable B shows the mass of the biocomposite after drying in the oven (grams).

Fig. 1. Water absorption test of biocomposite (Salas-Ruiz, 2019)

3. Results and Discussion

3.1. The effect of biodigester composition variations on the amount of chromium in water hyacinth substrate

The water hyacinth from the phytoremediation of tannery waste was processed using an anaerobic digestion method for 33 d to produce biogas and bio-slurry. The amount of chromium found in the bio-slurry was smaller than the amount of chromium in water hyacinth without an anaerobic digestion process. In Fig. 2, it is shown that the average chromium content in water hyacinth before anaerobic process was 21.277 mg/L, the average chromium content in the bio-slurry with a composition of 100% water hyacinth was 8.283 mg/L, and the average chromium content in the bio-slurry of 80% water hyacinth and 20% cow dung was 7.678 mg/L. This chromium reduction may occur due to the activity of microorganisms that can reduce the amount of chromium in the substrate during anaerobic digestion. According to the previous study by Gadd (1990), microorganisms can overcome high toxicity by several types of defense mechanisms, for example by precipitation of metals in their extracellular complex, metals transport via cell membrane, etc. Certain microorganisms can also reduce hexavalent chromium into trivalent chromium (Gadd, 1990). In this study, the measurement of the total amount of chromium was carried out using Atomic Absorption Spectrophotometry (AAS), so the valency of chromium could not be determined.

In testing the lignocellulose content of the substrate using the Chesson-Datta method (Winarno, 2004), an average ash value of 2.213% was obtained from 100% water hyacinth bio-slurry and 3.15% from 80% water hyacinth bio-slurry and 20% cow dung. The ash residue from the lignocellulosic content test of the substrate contains trace elements including toxic metal substances (Winarno, 2004). It can be assumed that the chromium from the water hyacinth substrate may be carried over to the ashing process therefore the chromium content showed in Fig. 2 does not exactly represent the loss of chromium in water hyacinth during anaerobic digestion process, but further research should be done to ensure this.

3.2. The effect of biodigester composition variations on changes in lignocellulose levels in water hyacinth substrate

In dry water hyacinth, there is an average hemicellulose content of 31%, an average cellulose content of 28.881%, and an average lignin content of 20.226%. As can be seen in Fig. 3, the lignin content in the bio-slurry with a composition of 100% water hyacinth was reduced to 17.503% while in bio-slurry with a composition of 80% water hyacinth the lignin was reduced to 18.110%. The hemicellulose content in the bio-slurry with a composition of 100% water hyacinth increased to 37.122% while in bio-slurry with a composition of 80% water hyacinth the hemicellulose increased to 35.321%. The cellulose content in the bio-slurry with a composition of 100% water hyacinth increased to 30.822% while in bio-slurry with a composition of 80% water hyacinth the cellulose increased to 29.197%. The reduction in the amount of lignin indicates that there might be a decomposition activity by microorganisms that happens during anaerobic digestion process, although it cannot be determined yet until further research has been conducted. There’s also an indication that the breakdown of the lignocellulose complex is incomplete because of the slight increase of hemicellulose and cellulose. Supposedly the decrease in the amount of cellulose and hemicellulose occurs in line with the decrease in the amount of lignin (Surthikanthi et al., 2005).

A reduction of lignin may occur because of the activity of the ligninolytic enzyme which breaks down lignin to produce phenolic compounds in the anaerobic digestion process. Lignin degradation occurs when the availability of easily metabolized substrates such as nitrogen, carbon, and sulfur is limited so that it is not sufficient for the growth of microorganisms. Lignin degradation can stop when the substrate is added with a nitrogen or carbon source that is easily metabolized (Costello and Chum, 2000). The amount of lignin in the 100% water hyacinth biodigester composition decreased more than the 80% water hyacinth biodigester composition and 20% cow dung, because of the assumption that the activity of ligninolytic-producing bacteria competes with other bacteria in the cow dung substrate. According to Suhut and Salundik (2012), the interaction between microbial groups in the substrate can also affect the anaerobic digestion process. The bacterial imbalance can affect the overall reaction rate in anaerobic digestion which can lead to inhibitor accumulation (Zhang, 2013). The addition of cow dung to water hyacinth can be assumed as a form of multiplication of the bacterial consortium in the biodigester.
so that it can cause an imbalance in bacterial activity. Further research should be conducted to determine the correlation between microbial activity in anaerobic digestion process and the reduction of lignin, hemicellulose, and cellulose of water hyacinths.

3.3. Biogas production

The biodigester with a composition of 100% water hyacinth produced an average volume of biogas of 0.236 L while the biodigester with a composition of 80% water hyacinth (WH) + 20% cow dung (CD) produced an average volume of 0.424 L of biogas (Table 4). This shows that the biogas produced from the addition of cow dung to the substrate water hyacinth was higher than biogas which was produced by water hyacinth substrate alone.

According to Forster-Carneiro (2008), the presence of a consortium of anaerobic and methanogenic bacteria in cow dung plays an important role in increasing biogas production at the methanogenesis stage. In the methanogenesis stage, there are two types of methane fermentation reactions. The first reaction is the change of acetic acid to methane and carbon dioxide, while the second reaction is the change of carbon dioxide and hydrogen into methane and water.

The metabolic activity of hydrolytic bacteria on organic substrates is influenced by the temperature and pH of the substrate in the biodigester. In Table 5, it is shown that the pH of the biodigester with a composition of 100% water hyacinth is in the range 7.19 - 7.38, while the pH of the biodigester with a composition of 80% water hyacinth is in the range 7.06 - 7.26. The pH value of cow dung is around 6.47 so it tends to be weakly acidic to neutral (Agus et al., 2014), but when mixed with water hyacinth substrate the pH tends to increase to around 7 (neutral to slightly alkaline) so that the activity of bacteria to decompose organic matter including the lignocellulose produced by bacteria which breaks down lignin more rapidly.

3.4. Analysis of biocomposite compressive strength test results as an alternative for roster base materials

The appearance of a biocomposite with a composition of 75% cement + 25% bio-slurry, biocomposite with a composition of 50% cement + 50% bio-slurry, and biocomposite with a composition of 25% cement + 75% bio-slurry, respectively.

The highest compressive strength was owned by the code 75C/25B biocomposite, which is 30.598 Mpa, with a composition of 75% cement and 25% bio-slurry (Fig. 6). In Table 2 it is shown that the more the addition of the amount of bio-slurry in the biocomposite composition, the less the compressive strength will be, as seen in the compressive strength values of the biocomposite codes 50C/50B and 25C/75B in Fig. 6.

Sample 75C/25B has the best compressive strength with a value of 30.598 Mpa. Sample 50C/50B also has good compressive strength with a value of 11.248 Mpa. These two values are meet the standard Quality I as recommended by SNI 03-0349-1989 with an average compressive strength of at least 10 Mpa which can be seen in Table 6 below. In Fig. 6, it is shown that the sample with code 100C/0B has a lower compressive strength than the sample with code 75C/25B. Sample 100C/0B was a control sample that was not given any addition of bio-slurry (100% cement and 0% bio-slurry).

The quality of biocomposite as a ventilation block is determined by the basic ingredients, additives, manufacturing process, and tools used for printing. According to Ginting (2005), the water-cement factor (FAS) will give the concrete maximum strength and density. The less cement water factor used in a mixture, the better...
the strength of the concrete (Intansari, et al., 2015). In Table 6, it is shown that the amount of water that binds to cement was less in the composition of 75C/25B, compared to the composition of 50C/50B and 25C/75B. This is because more amount of water was added to 50C/50B and 25C/75B to accommodate good hydration of the bio-slurry.

Table 4. Biogas volume

<table>
<thead>
<tr>
<th>Variations of biodigester composition</th>
<th>Biogas volume, l</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% WH</td>
<td>0.236</td>
</tr>
<tr>
<td>80% WH + 20% CD</td>
<td>0.424</td>
</tr>
</tbody>
</table>

Table 5. Substrate pH before and after anaerobic digestion for 33 d

<table>
<thead>
<tr>
<th>Variations of biodigester composition</th>
<th>Initial pH</th>
<th>Last pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% WH</td>
<td>7.19</td>
<td>7.38</td>
</tr>
<tr>
<td>80% WH + 20% CD</td>
<td>7.26</td>
<td>7.06</td>
</tr>
</tbody>
</table>

Fig. 6. Maximum compressive strength of biocomposites for each variation in composition

Fig. 7. Percentage of water absorption in the biocomposite for each composition variation

Table 6. Physical requirements of concrete bricks (SNI 03-0349-1989)

<table>
<thead>
<tr>
<th>Physical requirements</th>
<th>Unit</th>
<th>Quality of Solid Concrete Brick (Bata Beton Pejal)</th>
<th>Quality of Perforated Concrete Brick (Bata Beton Berlubang)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (minimum average value)</td>
<td>kg/cm²</td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>Minimum compressive strength value for each sample</td>
<td>kg/cm²</td>
<td>90</td>
<td>65</td>
</tr>
<tr>
<td>Maximum average value of water absorption</td>
<td>%</td>
<td>25</td>
<td>35</td>
</tr>
</tbody>
</table>

4. Conclusion

It can be concluded that the average chromium value found in bio-slurry resulted from the anaerobic digestion is smaller than the chromium value found in water hyacinths that didn’t undergo anaerobic digestion process. Therefore, anaerobic digestion is a promising method to reduce chromium levels found in post-phytoremediation water hyacinths. The biodigester with a composition of 80% water hyacinth + 20% cow dung produces an average biogas volume of 0.424 l, and this indicates the addition of cow dung to the water hyacinth substrate in anaerobic digestion process can produce the highest volume of biogas compared to the biogas produced by water hyacinths alone. From this study, we can also conclude that the biocomposite with the composition of 75% cement + 25% bio-slurry (sample code 75C/25B) has the best compressive strength value that adequate to Indonesian standard for materials (SNI). Therefore, biocomposite made of bio-slurry has the potential to be used as building alternative material, but further testing and experiment are still needed.

3.5. Analysis of biocomposite water absorption test results as alternative roster base materials

More addition of the amount of bio-slurry in the mixture of biocomposites resulted in a greater water absorption value, as can be seen in Fig. 7. In compositions of biocomposite that can be seen in Table 2, it is shown that the samples with the most bio-slurry composition had more paste too (25C/75B > 50C/50B > 75C/25B). The paste is a term used for a mixture of water and cement. This situation is by following the under the opinion of Troxell in Suroso (2001), that the condition of evaporation of water content in concrete can cause damage to the paste. The greater the amount of paste, the greater the damage caused by heating, so that the mortar becomes more porous and the water absorption becomes greater.

All samples 75C/25B, 50C/50B, and 25C/75B have the water absorption capacity that exceed the SNI-03-0349-1989 for quality I and quality II as can be seen in Table 6 above, which are 25% and 35%, respectively. Sample 75C/25B has the closest value to quality II with a value of 37.252% so that it has the potential to be tested again.
Conflict of interest

No potential conflict of interest was reported by the author.

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