Water Hyacinth Bioremediation for Ceramic Industry Wastewater Treatment-Application of Rhizofiltration System
(Biopemulihan Keladi Bunting untuk Industri Air Sisa Seramik
Aplikasi Perawatan Sistem Rizoturasan)

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ABSTRACT
In the present study, capability of water hyacinth in removing heavy metals such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Zinc (Zn), Iron (Fe), and Boron (B) in ceramic wastewater was investigated. The metal removal efficiency was identified by evaluating the translocation of metals in roots, leaves and shoot of water hyacinth. The heavy metal removal efficiency followed the order Fe>Zn>Cd>Cu>Cr>B during the treatment process. Water hyacinth had luxury consumption of those 6 elements. This study used the circulation system with 3 columns of plants which functioned as bioremediation of the sample. The concentration of metals in roots is much higher 10 times than leaves and stems. Roots give the result of metal >metal. The removal concentration from water hyacinth was estimated under pH of 8.21 to 8.49. This study proves water hyacinth to be a best plant for phytoremediation process.

Keywords: Ceramic wastewater; heavy metal removal; rhizofiltration; water hyacinth

INTRODUCTION
The production of bricks, clay and sand as raw material for ceramic industry has contributed to certain extent in the field of engineering. It has great recycle function especially in its wastewater usage, where cost has been reduced during formation of final product and environmentally safe due to waste handling (Garcia et al. 2011). However, it should be pointed that the ceramic industry also produces significant amount of wastewater that contains heavy metals. Studies have shown that the ceramic wastewater contains 15 mg/L of Boron and 2000 mg/L of suspended solids (Chong et al. 2009). Boron is widely used in the ceramic industry during the development of mechanical strength of tiles. In general, ceramic material is defined as inorganic materials, with possible organic content as well as non-metallic compounds. In addition, it produces a product with a small portion of clay which can be glazed or unglazed, porous or vitrified (Barros et al. 2007). A small amount of Boron and metallic elements in ceramic wastewater may affect plant tissues and human body.

It is well known that water hyacinth has the capability to absorb mineral compounds. Previous study has shown that it can remove up to 70% of chromium in wastewater (Keith et al. 2006) and absorb heavy metals such as cadmium and zinc (Henderson 2001). Water hyacinth is an exotic plant which can grow up to 3 feet and has green leave with sharp edges, circular to oval joined to a spongy reproduction. Water hyacinth grows well in many tropical and subtropical environments, which are some, become a problem. Fortunately, this also means that the region with those plants help rid their lakes and rivers of pollution (Saunders 2013).

Previous study has shown that metal up-take time and detention area plays an important role in phytoremediation, particularly its rhizofiltration (Stout & Nusslein 2010). Rhizofiltration is a filtration and absorption process of heavy metals by plant root over a specific period of time.

In the present study, capability of water hyacinth in removing heavy metals such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Zinc (Zn), Iron (Fe), and Boron (B) in ceramic wastewater was investigated. The metal removal efficiency was identified by evaluating the translocation of metals in roots, leaves and shoot of water hyacinth. The heavy metal removal efficiency followed the order Fe>Zn>Cd>Cu>Cr>B during the treatment process. Water hyacinth had luxury consumption of those 6 elements. This study used the circulation system with 3 columns of plants which functioned as bioremediation of the sample. The concentration of metals in roots is much higher 10 times than leaves and stems. Roots give the result of metal >metal. The removal concentration from water hyacinth was estimated under pH of 8.21 to 8.49. This study proves water hyacinth to be a best plant for phytoremediation process.

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Response of a plant to hydraulic retention time (HRT) is also considered due to availability of water to retain pollutant. Accordingly, the current treatment method was selected based on economic point of view and this application may execute in situ plants which grow on ceramic wastewater surface.

Even though a number of studies have been conducted on phytoremediation, there were not many studies on ceramic wastewater treatment using water hyacinth. Accordingly, the aim of this study was to investigate heavy metal removal from ceramic wastewater using water hyacinth. The heavy metals investigated were Cadmium (Cd), Chromium (Cr), Copper (Cu), Zinc (Zn), Iron (Fe), and Boron (B). A batch analysis using continuous rhizofiltration system (Minhee & Minjune 2010) was investigated to remove heavy metals from ceramic wastewater. In addition, psychological response of plant portion to heavy metals absorption and its synchronization to their food was also assessed.

MATERIALS AND METHODS

REMEDIATION USING SINGLE PLANT

Water hyacinth was collected from a Nursery in Skudai, Johor Bharu, Malaysia. The seedling was cultivated using water in a Hydroponic basin (10 L) for a period of 3 days. Ceramic wastewater was collected from a local ceramic factory (Table 1). For each batch analysis, around 400 mL of ceramic wastewater was used. The purpose of batch analysis was to ensure adaptability of plant to ceramic wastewater and to cultivate growth. Plant size and weight was determined regularly to choose the best plant for experiment. Later, primary study was performed in 20 L Hydroponic container to investigate heavy metal removal from the ceramic wastewater. In general, around 8 to 11 plants of water hyacinth were specified. The preliminary and primary studies were then performed at 12, 24, 48, and 72 h of retention time.

EXPERIMENTAL SETUP

Generally, the present study focused on adsorption by root and it is considered as a tertiary treatment of wastewater. A 3-phase cleaning system, with constant flow rate passing through the 3 columns with different root lengths and distance from first holding tank was proposed for the study, in order to maintain suitable loading and flow rate which consisted a retention pond and rhizofilter. Figure 1 shows the experimental set-up of the study. All variables were identified initially and wastewater was circulated in one direction in the container (0.28 × 0.19 × 0.46 m). Arithmetic mean for the removal efficiency was used when deviation was within 30% of the mean (Lee & Yang 2010). The experiment was performed by first feeding the ceramic wastewater into a holding tank (0.024 m$^3$) for a period of time. Subsequently, the wastewater was fed into 1st column, followed by column 2 and 3 containing water hyacinth for 5 days. Lastly, the effluent from column 3 was fed back to holding tank.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH</td>
<td>-</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>DO</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td>Chemical Oxygen demand</td>
<td>COD</td>
<td>822 ± 42.0</td>
</tr>
<tr>
<td>Total Suspended Solid</td>
<td>TSS</td>
<td>0.181 ± 0.11</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>14.4 ± 0.20</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>20 ± 0.11</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>8.13 ± 0.25</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>1.51 ± 0.10</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>19.25 ± 0.02</td>
</tr>
</tbody>
</table>

FIGURE 1. Schematic diagram of experimental flow (units in m)
Since rhizofiltration focuses on root system, it is vital to investigate metal accumulation in the root, shoot and leaves of the water hyacinth. Each water hyacinth plant was separated and washed 3 times using distilled water before drying in oven for 2 days. In order to study the accumulation of heavy metals in plants, the concentration of heavy metals was analyzed in roots, stems and leaves of plants (Asheesh et al. 2012).

Laboratory experiments were conducted on samples taken from each basin. This study was conducted for 5 days. Experiments carried out at the beginning of the study, until 5th day with rhizofilter circulation system. Control tests without plant materials were carried out to consider the non rhizofiltration effects in batch experiments. The process of treatment is basically without any circulation with free flow condition.

**RESULT AND DISCUSSION**

**THE PERFORMANCE OF METALS**

The early concentration of influents in this treatment is stated in Table 1. The overall performances of metals can be seen in Table 2. Figure 2 shows the Boron reduction profile in each column of the treatment system. It can be seen that Boron concentration decreased sharply from 14.4 mg/L to around 3.6 mg/L (75% removal efficiency), confirming the removal of Boron by water hyacinth. Boron was successfully absorbed by water hyacinth through reaction for growth. It is generally known that plants need around 0.3 to 1.0 mg/L of Boron for growth (Weiner 2012). As for Copper removal rate, it can be seen that it was reduced tremendously, from 20 to 2.4 mg/L in the effluent, confirming again the effectiveness of water hyacinth in removing heavy metals from ceramic wastewater (Figure 3). Copper is absorbed by water hyacinth to strengthen its cell and encourages metabolism of nitrogen and carbohydrate in the photosynthesis process (Hammad 2011).

Figure 4 shows Zinc reduction profile, where 97% removal efficiency was noted during the operational period. The stem structure of water hyacinth promotes excellent absorption capacity for growth. Zinc activates enzymes for protein synthesis and can be used as starch production and root growth for water hyacinth (Mufarrege et al. 2010).

Iron is an important element for plant growth and it is generally absorbed by roots by rhizofiltration process. Plants have fibrous root which makes the rhizofiltration process easier (Nedelkoska & Doran 2000). Plants needed this element for enzyme formation that can help photosynthesis. As shown in Figure 5, the Iron removal efficiency increased uniformly from day 3 to 5, with up to 99% removal rate.

As for the Chromium removal, water Hyacinth showed promising results as a hyper-accumulator. The water hyacinth appeared to be a good choice for removing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>Effluent</th>
</tr>
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<tbody>
<tr>
<td>B, mgL⁻¹</td>
<td>3.40</td>
<td>23.6</td>
<td>10.37</td>
<td>72.0</td>
<td>10.90</td>
</tr>
<tr>
<td>Cu, μgL⁻¹</td>
<td>7.50</td>
<td>37.5</td>
<td>15.00</td>
<td>75.0</td>
<td>15.66</td>
</tr>
<tr>
<td>Zn, mgL⁻¹</td>
<td>5.13</td>
<td>63.1</td>
<td>7.92</td>
<td>97.4</td>
<td>7.72</td>
</tr>
<tr>
<td>Fe, mgL⁻¹</td>
<td>1.07</td>
<td>71.2</td>
<td>1.48</td>
<td>98.2</td>
<td>1.48</td>
</tr>
<tr>
<td>Cr, mgL⁻¹</td>
<td>13.24</td>
<td>68.8</td>
<td>16.53</td>
<td>85.9</td>
<td>16.26</td>
</tr>
<tr>
<td>Cd, mgL⁻¹</td>
<td>0.10</td>
<td>62.3</td>
<td>0.10</td>
<td>64.8</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**FIGURE 2, Boron removal profile in each column during the treatment of ceramic wastewater using water hyacinth.**
chromium from polluted water. At low concentrations, the plant removed about 70% of the chromium in the water. As the concentrations increased, the plant appeared not able to absorb as much chromium, as the removal rate was around 25%. It can be seen that up to 83% chromium was removed compared to control (68%), as shown in Figure 6.

One of the main toxic effects of Cadmium in plants is growth reserve in size and in dry weight of tops and roots (Benavides et al. 2005). Water hyacinths showed only a minimal negative impact from cadmium exposure, because of the needs and important of nutrient source. Cadmium removal efficiency was 96% (Figure 7).
Table 3 shows the chemical analysis in each column during the treatment of ceramic wastewater using water hyacinth. It can be seen that the pH in the two plants was neutral pH (Control). This shows that installation of water hyacinth with ceramic wastewater can improve pH to neutral, better than the control. pH experiments showed that the ceramic wastewater varies between alkaline and neutral within the treatment period due to chemical reactions that occur during the retention performance (pH of 8.49).

Environmental contaminant which is caused by toxic heavy metals along with high chemical oxygen demand (COD) load in industrial wastewater is a common problem. Effluents begin from industry contain loads of organic pollutants much higher than the permissible discharge limit. Prabir et al. (2010) demonstrated combination of electro-Fenton process and chemical precipitation was used to treat rayon industry wastewater and reduce its chemical oxygen demand (COD). Results obtained with industrial wastewater having a reduction COD of 88% in 50 min. The increment of COD value at the first day treatment, 853 mgL⁻¹ with influent reading, 822 mgL⁻¹ is also mainly because of the admixture with existing organic material on the process of wastewater sample and plants relocation. However, after the first day of treatment, the COD value are decreased by day after day until the last fifth day, 101 mgL⁻¹. The value of DO for the three sets of plants was convergence decreased to the 6.52 mgL⁻¹. After that, DO experience phase fluctuations in small rate. On the fifth day of treatment, it can be seen that the value of DO are increased day after day. Oxygen in the sample is used for the decomposition of organic matter by bacteria in the process of aerobic respiration. In addition, the roots of the plant are the medium that can make the process of aerobic decomposition can occur more effectively (Narendranathan 2004). Total suspended solid (TSS) values for the three sets of water samples were shown in Table 3. Based on this table, the average value for all sets of TSS decreased from 0.181 to 0.03 gmL⁻¹ significantly throughout the treatment. This is due to the solid sediments at the base sample in basin due to gravity forces during the study. However, can be seen in every experiment performed at each period of detention, water hyacinth has a lower TSS values. This is
because as well as the action of gravity, water hyacinth plant roots, thick and has a high total surface area allows it suspended solid trap contained in the ceramic waste water properly.

**WATER HYACINTH PERFORMANCES**

Water hyacinth length, weight, stem and leave width was determined (Table 4), in order to investigate its growth rate. Long heavily roots were seen to increase up to 0.16 cm within 5 days of treatment. Length varies from 4 to 15 cm in small plants, 10 to 36 cm in medium plants and 12 to 22 cm, in large plants. Water hyacinth takes in the range 6 and 28 days to double in weight and between 4 and 58 days to double in number based on field dimensions (Zanxin & Margaret 2012). At certain situations, its populations could be doubled within two weeks. Due to copper contaminations in the ceramic wastewater, the growth rate of water hyacinth was limited to certain extend. Based on Table 4, in general, roots length showed some increment (0.58±0.2 cm), while, leave and stem 0.38±0.13 cm and 0.43±0.13 cm (average). Weight of water hyacinth also showed some increment (27.96 to 37.1 g in C1), signifying growth of water hyacinth during the treatment of ceramic wastewater. Scanning electron microscope (SEM) showed that the roots were covered with large fragments of heavy metals (Figure 8(b)), suggesting that absorption were the main mechanisms in the treatment process containing ceramic wastewater by rhizofiltration.

**CONCLUSION**

Phytoremediation of wastewater through rhizofiltration has the ability to trap and filter contaminants such as metals and organic pollutants. The circulation process in the current study contributed to a best mechanism for the treatment of heavy metals in the ceramic industry, whereby it give simple technique, natural process and low cost method. Water hyacinth is appropriate and suitable hyper accumulator for the treatment of ceramic wastewater.

<table>
<thead>
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<th>Effluent</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>8.45 ± 0.1</td>
<td>8.49 ± 0.03</td>
<td>8.49 ± 0.20</td>
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<tr>
<td>DO</td>
<td>mgL⁻¹</td>
<td>6.71 ± 0.07</td>
<td>6.82 ± 0.15</td>
<td>6.19 ± 0.01</td>
<td>6.52 ± 0.82</td>
</tr>
<tr>
<td>COD</td>
<td>mgL⁻¹</td>
<td>160 ± 8</td>
<td>135 ± 9.0</td>
<td>124.7 ± 445</td>
<td>101.7 ± 9.35</td>
</tr>
<tr>
<td>TSS</td>
<td>gml⁻¹</td>
<td>0.02 ± 0.01</td>
<td>0.04 ± 0.01</td>
<td>0.02 ± 0.05</td>
<td>0.03 ± 0.01</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
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<th>C1</th>
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<th>C1</th>
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<th>C3</th>
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<tr>
<td>Root length, cm</td>
<td>6.12</td>
<td>4.23</td>
<td>4.35</td>
<td>6.73</td>
<td>4.97</td>
<td>4.73</td>
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<tr>
<td>Leave width, cm</td>
<td>5.61</td>
<td>5.78</td>
<td>5.32</td>
<td>6.01</td>
<td>6.15</td>
<td>5.83</td>
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<tr>
<td>Stem width, cm</td>
<td>2.37</td>
<td>2.11</td>
<td>2.02</td>
<td>2.91</td>
<td>2.56</td>
<td>2.32</td>
</tr>
<tr>
<td>Weight, g</td>
<td>27.96</td>
<td>15.97</td>
<td>17.83</td>
<td>37.1</td>
<td>17.25</td>
<td>22.18</td>
</tr>
</tbody>
</table>

**FIGURE 8.** Scanning electron microscope (SEM) images of the surface of the sunflower root (a) before and (b) after rhizofiltration.
wastewater containing iron, cadmium, chromium, zinc and boron. In this study, water hyacinth was able to remove more than 70% of heavy metals in ceramic wastewater. The production of food using accumulator water hyacinth to farm is the future study that will compact in 3R’s application.

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REFERENCES

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