ABSTRACT

Unvegetated constructed wetlands of lab-scale were employed to treat the phosphorus of landfill leachates. Media of variation types, namely gravel, a mixture of gravel and charcoal powder in 2:1 ratio, a mixture of gravel and granular charcoal in 2:1 ratio, and a mixture of gravel and granular charcoal in 1:1 ratio were used to fill up the constructed wetland units (Reactors) I, II, III, and IV, respectively. Sample of untreated landfill leachate collected from landfill site of Pulau Burung in Penang, was introduced into the reactors. The first trial was conducted as single and two-cycle system; nonetheless the following trial for phosphorus analysis was only conducted as single cycle system. The total reactive phosphorus (TRP) removal obtained at the end of the single cycle was 34.10, 47.50, 75.00, and 54.00 % for Reactor I, II, III, and IV, respectively. At the end of two-cycle, the presence of charcoal showed the negative effect on TRP removal. The results of this study indicated that the sorption of phosphorus to the media was not infinite but approaches sorption capacity at phosphorus addition.

Keywords: Constructed wetland, phosphorus, landfill leachates

INTRODUCTION

Wetlands are an ecotone – an “edge” habitat, a transition zone between dry land and deep water, an environment that is neither clearly terrestrial nor clearly aquatic [1]. Wetlands vary widely because of regional and local differences in soils, topography, climate, hydrology, water chemistry, vegetation, and other factors including human disturbance. Indeed, wetlands are found from the tundra to the tropics and on every continent except Antarctica [2].

The multiple functions and values of wetlands have only recently begun to be recognized. The following are functions and values of wetlands, as recognized by the Wetland Evaluation Technique currently used by the U.S. Army Corps of Engineers and other agencies [3]:

Functions: (which may also be considered values to some)
- Groundwater recharge and discharge,
- Floodwater alteration, sediment stabilization and sediment/toxicant retention, nutrient removal/ transformation, production export,
- Aquatic and wildlife diversity/ abundance

Values: (which do not perform functions within the wetland)
- Recreation, uniqueness/heritage value

Wetlands can effectively remove or convert large quantities of pollutants from point sources (municipal and certain industrial wastewater effluents) and non point sources (mine, agricultural, and urban runoff) including organic matter, suspended solids, metals, and excess nutrients [1].

Constructed wetlands, because of their ecosystem characteristics that are similar to natural wetlands, are generally accepted as an ecotechnology for treatment of various types of wastewaters. It offers a wide spectrum of natural processes that may serve to reduce leachate contaminants [4].

Many constructed wetlands do not appear, however, to effectively remove phosphorus from wastewater. The problem of maximizing long-term high efficiency of phosphorus retention in engineered wastewater-wetland system is based on our lack of understanding of the most efficient pathways which can move phosphorus from the available form in the water column or soils pore water into a permanent sink as well as our inability to predict the desorption or release of phosphorus from unavailable forms to soluble phosphorus in the environment [5].

Several studies have shown that immobilization of phosphorus in constructed wetlands occurs through substratum adsorption, chemical precipitation, bacterial action, plant and algal uptake and incorporation into organic matter [6]. Phosphorus may also be bound to the media of the reed bed mainly as a consequence of
adsorption and precipitation reactions with calcium (Ca), aluminum (Al) and iron (Fe) in the sand or gravel substrate, which are potentially very stable in the soil, affording long-term storage of phosphorus [7-8].

Adsorption and precipitation of phosphorus in wastewater treatment wetlands is considered to be sort-term and finite [5]. Once phosphorus is adsorbed onto the soil solid phase, it may undergo biological transformations into organic forms, which may enhance the immobilization of phosphorus. So, the quantitative description of phosphorus adsorption onto the solid phase of the soil is important as an initial phase in the determination of its ability to remove phosphorus from wastewater [9]. Since adsorption and precipitation have become saturated, the wastewater treatment wetlands reach phosphorus storage capacity and no longer function effectively for phosphorus removal. This has been referred to as the “aging phenomena” in wetlands that receive wastewater [5].

Performances of different filter media of constructed wetlands were not compared systematically in the literature reports. This study was to compare the phosphorus removal efficiency for charcoal added constructed wetland filter media treating landfill leachate.

**EXPERIMENTAL SECTION**

Four constructed wetland reactors were built with dimension of 29 cm wide, 40 cm long, and 35 cm depth. The depth of the filter media for all reactors was the same at 30 cm. The inlet and outlet tap ports were built approximately half of the media height while outlet overflow was at the same level of the media surface. The media consist of gravel, granular charcoal, and charcoal powder with size ranges of 2 < Ø < 5 mm, 2 < Ø < 5 mm, and Ø < 2 mm, respectively.

The media (gravel, granular charcoal, and charcoal powder) were characterized includes moisture, pH, and acid extractable phosphorus. The surface area and CHN ratio of the charcoal was also determined.

**Table 1.** Constructed wetland unit (Reactor) specification

<table>
<thead>
<tr>
<th>Reactor</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of media</td>
<td>Gravel, 100%</td>
<td>Gravel : Charcoal = 2 : 1</td>
<td>Gravel : Charcoal = 2 : 1</td>
<td>Gravel : Charcoal = 1 : 1</td>
</tr>
<tr>
<td>Gravel capacity</td>
<td>30 L</td>
<td>24 L</td>
<td>21 L</td>
<td>16 L</td>
</tr>
<tr>
<td>Charcoal capacity (powder)</td>
<td>-</td>
<td>12 L</td>
<td>11 L</td>
<td>16 L</td>
</tr>
<tr>
<td>Charcoal capacity (granule)</td>
<td>-</td>
<td>(granule)</td>
<td>(granule)</td>
<td></td>
</tr>
<tr>
<td>Total media</td>
<td>30 L</td>
<td>36 L</td>
<td>32 L</td>
<td>32 L</td>
</tr>
<tr>
<td>Capacity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow rate (mL/min)</td>
<td>1.76</td>
<td>1.76</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>HRT (days)</td>
<td>5.05</td>
<td>4.25</td>
<td>5.3 days</td>
<td>5.75</td>
</tr>
</tbody>
</table>

Prior to apply media into reactors, the media was washed thoroughly first by immersing in hydrochloric acid (1:9 v/v) for 24 hours, and later rinsed with tap water until pH neutral. Composition and capacity of media in reactors, flow rate and hydraulic retention time (HRT) for leachate sample are given in Table 1.

Sample of untreated landfill leachate used in this study was collected from of Pulau Burung Landfill, Penang. The leachate sample was introduced into four types of reactors, which were placed in indoor laboratory.

The First Trial was conducted as single and two-cycle system during September 17th – October 2nd 2002. Landfill leachate was treated by using laboratory-scale unvegetated constructed wetlands subsurface-flow system (Reactor I-IV). Each Reactor operation (HRT = 4.25-5.75 days) was repeated twice consecutively resulting in a total cycle time of about 8.5-11.5 days. Both phosphorus (TRP) level from inlet and outlet overflow wereanalysed at the end of single and two-cycle system.

The following trials were conducted as single cycle system. The Second Trial was run during February 10th – 24th and the Final Trial was run in August 9th – 23rd 2003. Leachate samples for the analysis were collected at the interval of two days. Phosphorus (total, suspended, and soluble reactive phosphorus) concentration from inlet, outlet tap, and outlet overflow were analysed according to the Standard Methods for the Examination of Water and Wastewater [10]. Phosphorus (total, acid-hydrolysable, and reactive) concentration during the Final Trial also were analysed according to the Standard Methods for the Examination of Water and Wastewater. The temperature and pH also were monitored.

Biofilm sample on constructed wetland (Reactor I and III) filter media (gravel and charcoal) surfaces for analysis by SEM was prepared by fixation of samples in osmium tetroxide followed by dehydration using critical point drying with liquid nitrogen, and coating of biofilm with ≈ 20 nm gold using Polaron SC 515 sputter coater.

**RESULT AND DISCUSSION**

**Filter Media Characterization**

The filter media was characterized in the laboratory. Characterization regarding the media, some of their properties determined are given in Table 2.

The diameter of gravel and granular charcoal were 2 – 5 mm. It was intended to minimize the risk of clogging phenomenon. However, since the BET Surface Area of charcoal powder (Ø < 2 mm) was more two times greater than granular charcoal, it was necessary to study and compare the performances of powdered and granular charcoal added in constructed

Pedy Artsanti, et al.
Table 2. Filter media characterization

<table>
<thead>
<tr>
<th>Properties of Media</th>
<th>Gravel</th>
<th>Charcoal (granule)</th>
<th>Charcoal (powder)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size/diameter</td>
<td>2-5 mm</td>
<td>2-5 mm</td>
<td>&lt;2 mm</td>
</tr>
<tr>
<td>Moisture</td>
<td>(7.61x10^2) ± 0.01 %</td>
<td>6.6 ± 0.09 %</td>
<td>5.5 ± 0.21 %</td>
</tr>
<tr>
<td>BET surface area</td>
<td>-</td>
<td>0.3731 sq m g^-1</td>
<td>0.8733 sq m g^-1</td>
</tr>
<tr>
<td>C : H : N</td>
<td>-</td>
<td>60.48 : 6.26 : 0.2</td>
<td>72.22 : 4 : 0.08</td>
</tr>
<tr>
<td>pH</td>
<td>5.18</td>
<td>4.75</td>
<td>4.57</td>
</tr>
<tr>
<td>Acid extractable phosphorus</td>
<td>6.93 ± 1.00 mg L^-1</td>
<td>1.23 ± 0.00 mg L^-1</td>
<td>1.47 ± 0.03 mg L^-1</td>
</tr>
</tbody>
</table>

wetland filter media treating landfill leachate. Theoretically, the larger BET Surface Area provides the higher degree of adsorptive capacity for the pollutants. However, it was commonly revealed by the finer particle size diameter, increasing the risk of clogging phenomenon.

The pH of the media was 5.18, 4.75, and 4.57 for gravel, granular charcoal, and powdered charcoal, respectively. In acid soils, inorganic phosphorus is adsorbed on hydrous oxides of Fe (Iron) and Al (Aluminium) and may precipitate as insoluble Fe-phosphates and Al-phosphates [5]. However, in this case apparently the pH of the media showed no significant effect on the treatment of landfill leachate during experimental period.

Since the adsorption and precipitation of phosphorus in wastewater treatment wetlands is considered to be finite, it is important to determine the amount of native phosphorus of the media. The acid extractable phosphorus of the media were 6.93, 1.23, and 1.47 mg L^-1 for gravel, granular charcoal, and charcoal powder, respectively. The high amount of native phosphorus of the gravel media mainly as a consequence of the presence of Ca, Al, and Fe in the gravel substrate that provided Ca-phosphate, Al-phosphate, and Fe-phosphate [5,7,9].

**Total reactive phosphorus (TRP) removal in single and two-cycle system**

The result of the First Trial of TRP removal study is discussed below. The TRP concentration of inlet and outlet overflow at the end of the single and two-cycle are depicted in Figure 1. The final TRP concentration of outlet overflow of Reactor I obtained at the end of single cycle was 4.22 mg L^-1 resulting in 34.10 % TRP removal. Percent TRP removals for the same single cycle were 47.50, 75.00, and 54.00 % resulting in final TRP concentration of 3.44, 6.00, and 4.10 mg L^-1 for outlet overflow of Reactor II, III, and IV, respectively. It seems that the presence of charcoal as substrate-media in Reactor II, III, and IV have removed TRP more efficiently than only gravel in Reactor I. On the contrary, at the end of two-cycle the presence of charcoal showed the negative effect on TRP removal, especially in Reactor II and III. This phenomenon indicated that increasing the number of cycles did not improve TRP removal of landfill leachate by using this system. The phosphorus sorption processes are reversible, and hence release of phosphorus can be observed from phosphorus-containing media if loaded with a low concentration of phosphorus in wastewater [11]. This was probably the reason of release of phosphorus in two-cycle system. In addition, the phosphorus removal efficiency is often high initially and then decreases after some time as the phosphorus-sorption capacity of the substrate-media is used up [7].

**Media effectiveness for phosphorus removal**

The Second Trial experiment results for phosphorus concentration before and after treatment in unvegetated constructed wetland subsurface-flow systems are shown in Table 3 and 4. From those tables, it shows that more than 50 % of landfill leachate reactive phosphorus was in soluble form. The removal process of total and soluble reactive phosphorus provided the negative effect. Arias et al. [11] also observed similar results in their study. Since the reactor reached phosphorus storage capacity, no removal was revealed and leaching phenomenon was occurred.

Furthermore, Tables 3 and 4 shows the released phenomenon of phosphorus at outlet tap and outlet overflow. The total and soluble reactive phosphorus concentrations of outlet tap, in average, were higher than that of outlet overflow for all of the reactors. Apparently, anaerobic condition of the zone of outlet tap was contributed to provide this phenomenon. Schön et al. [12] reported that at a limiting content of dissolved oxygen, phosphate uptake would probably still occur on the surface of the media, while in the interior, phosphate is released. Converti et al. [13] also pointed out that phosphorus was released in anaerobic condition.

According to Table 3, outlet overflow TRP concentration in average, were 4.98, 7.26, 7.70, and 8.79 mg L^-1 for Reactor I, II, III, and IV, respectively. Reactor I, which contain only gravel shows the lowest concentration of released phosphorus. The other three reactors, which also contain some portion of charcoal however provide worse performance of inhibit phosphorus release during the Second Trial.

The same trend was demonstrated by the soluble reactive phosphorus data from Table 4. Since the studies indicate that aluminium (Al), iron (Fe), and calcium (Ca) in gravel substrate are strong adsorbent of phosphorus [7,14], the capability of a reactor to remove phosphorus may therefore be dependent on

Pedy Artsanti, et al.
Table 3 Total reactive phosphorus

<table>
<thead>
<tr>
<th>Constructed Wetland Unit (Reactor)</th>
<th>Inlet range</th>
<th>Inlet average</th>
<th>Outlet tap range</th>
<th>Outlet tap average</th>
<th>Outlet over flow range</th>
<th>Outlet over flow average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor 1</td>
<td>3.8-5.1</td>
<td>4.31 ± 0.54</td>
<td>3.8-7.3</td>
<td>5.48 ± 1.29</td>
<td>3.4-6.4</td>
<td>4.98 ± 0.95</td>
</tr>
<tr>
<td>Reactor 2</td>
<td>3.5-6.1</td>
<td>4.62 ± 0.99</td>
<td>5.2-10.2</td>
<td>8.61 ± 1.7</td>
<td>5.4-8.9</td>
<td>7.26 ± 1.21</td>
</tr>
<tr>
<td>Reactor 3</td>
<td>3.4-5.3</td>
<td>3.99 ± 0.69</td>
<td>9.1-9.8</td>
<td>9.45 ± 0.26</td>
<td>6.8-8.8</td>
<td>7.7 ± 0.64</td>
</tr>
<tr>
<td>Reactor 4</td>
<td>3.7-4.8</td>
<td>4.39 ± 0.43</td>
<td>5.4-10.8</td>
<td>9.38 ± 2.01</td>
<td>5.4-10.2</td>
<td>8.79 ± 1.69</td>
</tr>
</tbody>
</table>

*Note: all values in mg L⁻¹*

Table 4 Soluble reactive phosphorus

<table>
<thead>
<tr>
<th>Constructed Wetland Unit (Reactor)</th>
<th>Inlet Range</th>
<th>Inlet average</th>
<th>Outlet tap Range</th>
<th>Outlet tap average</th>
<th>Outlet over flow Range</th>
<th>Outlet over flow average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor 1</td>
<td>2.0-2.5</td>
<td>2.32 ± 0.16</td>
<td>1.6-6.0</td>
<td>3.64 ± 1.55</td>
<td>2.2-4.3</td>
<td>2.74 ± 0.76</td>
</tr>
<tr>
<td>Reactor 2</td>
<td>1.8-2.6</td>
<td>2.32 ± 0.29</td>
<td>3.8-10.1</td>
<td>8.14 ± 2.16</td>
<td>4.7-7.6</td>
<td>5.79 ± 1.06</td>
</tr>
<tr>
<td>Reactor 3</td>
<td>2.0-2.6</td>
<td>2.30 ± 0.23</td>
<td>9.0-9.6</td>
<td>9.32 ± 0.24</td>
<td>5.1-8.4</td>
<td>6.93 ± 0.98</td>
</tr>
<tr>
<td>Reactor 4</td>
<td>2.0-2.7</td>
<td>2.32 ± 0.17</td>
<td>4.9-10.6</td>
<td>9.15 ± 2.14</td>
<td>4.8-10.0</td>
<td>8.41 ± 1.80</td>
</tr>
</tbody>
</table>

Fig 1. Influent and effluent of TRP concentration for Reactor I-IV at the end of the single and two-cycle operation.

Fig. 2. Suspended Reactive Phosphorus for Reactor I-IV

Figure 3. SEM image of biofilm formed on the surface of the media (2500 x magnification); Biofilm on the surface of gravel (upper); Biofilm on the surface of charcoal (lower)
the contents of these minerals in the substrate-media. The presence of charcoal as substrate-media inside the reactor reduced the gravel volume. There the content of Al, Fe, and Ca decreased in significant amount, provided lower storage capability of phosphorus. This is in agreement with the result of acid extractable phosphorus of gravel and charcoal in Table 2. From all of the statement above, it is clear that the presence of charcoal could not increase the phosphorus storage capability of the media.

The result of suspended reactive phosphorus for Reactor I, II, III, and IV was depicted in Figure 2. In contrast with the phenomenon of total and soluble reactive phosphorus removal, the presence of charcoal in Reactor II, III, and IV provided the better performance than only gravel in Reactor I on the removal of suspended reactive phosphorus. Apparently the main mechanisms for the removal of suspended reactive phosphorus were presumed to be by filtration, adsorption, precipitation, and sedimentation [15]. The highest performance was observed in Reactor IV. It seems that the charcoal adding up to 50 % of total volume of reactor provided significant effect of improvement on the performance of suspended reactive phosphorus removal.

Assessment of phosphorus removal

According the results of the Second Trial, all of the reactors seemed already exhausted for phosphorus removal. Therefore, the final trial considered to run in August 2003 to give some rest on the treatment of landfill leachate for the reactors. The results of the last trial are shown in Figure 4 and 5 (a) and (b).

Figure 4 shows the phosphate fraction that consists of organic phosphorus, acid-hydrolysable phosphorus, and reactive phosphorus. It can be seen from that figure, the organic phosphorus fraction did not exist in the inlet, otherwise it exist in significant amount at outlet port, both tap and overflow. The organic phosphorus apparently formed from orthophosphate in biological processes [10]. Since the biofilm exist on the media surfaces (Figure 3), it is generally believed that the biological processes must be occurred during this experiment. Accumulation of microorganisms on surfaces as biofilms often enhances the potential for biotransformation of contaminants. The rate of biotransformation is strongly influenced by porous media mass transport characteristics including media permeability and pore velocity distribution, as well as by biofilm surface roughness and other variables that affect the delivery rate of substrate and nutrients to growing cell [16]. Since the biofilm surface roughness formed on the gravel surfaces was different with the biofilm formed on the granular charcoal surfaces, the rate of biotransformation of the reactors during the treatment of the leachate also different [15].

From Figure 4, it is shown that the acid hydrolysable phosphorus fraction was removed during the trial. Otherwise, the presence of charcoal in the Reactor III did not improve the removal of this phosphorus fraction. Apparently it is due to the decreased of the calcium (Ca), aluminum (Al) and iron (Fe) content in the media as a consequence of the presence of charcoal in Reactor III.

The major fraction of phosphorus is reactive phosphorus that contains 84.02 and 86.59 % of total phosphorus for inlet of Reactor I and III, respectively. From Figure 4, it can be observed that the reactive phosphorus
phosphorus removal significantly occurred in outlet overflow of both reactors. While at the outlet tap of Reactor III the removal did not occur. As discussed in Section 3, the aerobic and anaerobic condition of the outlet zone apparently was the important factor influenced the reactive phosphorus removal in this experiment. In addition, although the organic phosphorus formed during the treatment was relatively low, apparently it was also contributed to the decrease of the phosphorus removal efficiency.

The TRP removal of Reactor I and III were monitored during the Final Trial and the results was shown in Figure 5. From that figure, it can be observed that there is no significant difference between the TRP concentrations of inlet and outlet tap from both of the reactors. These results confirmed that the TRP removal did not occur at the outlet tap, which provided anaerobic zone of the reactors. On the contrary, the outlet overflow of both reactors which provided aerobic zone revealed the significant amount of TRP removal during this final trial.

Further more, from Figure 5, it is shown that the TRP concentration of outlet overflow increase significant amount at the end of the trial. The inlet concentrations of TRP were relatively high with average value of 10.65 and 11.58 mg L\(^{-1}\) for Reactor I and III, respectively. This relatively high phosphorus loading applied to these two reactors might be the cause of lower removal efficiencies at the end of the trial. This phenomenon indicated that the sorption of phosphorus to the media is not infinite but approaches sorption capacity at phosphorus additions. The same phenomenon of this experiment was observed by Søvik and Kløve [17]. It was believed that most of the amounts of TRP removed from the non-vegetation constructed wetland systems were achieved by chemical adsorption. This is in agreement with the observation made by Yang et al. [18].

CONCLUSION

In the First Trial, it indicated that increasing the number of cycles of treatment process did not improve TRP removal. In the following trial for the similar parameter, the removal process of total and soluble reactive phosphorus provided the negative effect. Results of this study indicated that the sorption of phosphorus to the media was not infinite but approaches sorption capacity at phosphorus additions. Most of the amounts of TRP removed from this system were achieved by chemical adsorption.

ACKNOWLEDGEMENT

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REFERENCES


