Treatment of eutrophic lake water and phosphorus recovery by reusing alum sludge and/or wood

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ABSTRACT

Treatment of eutrophic lake water was investigated, when alum sludge and/or wood were used as the media for laboratory-scale filtration. Process 1 consisted of Column 1 with wood and Column 2 with alum sludge in series, and Process 2 of Column 3 with alum sludge. The filtration velocity was 0.45 and 0.91 m/d for 49 days each. Both processes removed suspended solids and total phosphorus well with about 98% and 92% removal efficiency, respectively. Total nitrogen removal efficiency was higher in Process 1 (64–72%) than Process 2 (18–19%), because of biological denitrification using organics supplied from wood. The dissolution of organics and aluminium from wood and alum sludge, respectively, was not significant in the effluent. An alkaline extraction method was able to extract two-thirds of phosphorus in the alum sludge. Thus, alum sludge was excellent at removing and recovering phosphorus and the filtration combining wood and alum sludge enabled the concomitant removal of nitrogen and phosphorus.

Key words | alum sludge, denitrification, lake water, phosphorus recovery, wood

INTRODUCTION

Serious eutrophication problems have prevailed in closed water bodies all around the world. Although reducing pollutant loads should be taken first among many remedial options, it takes time to fully develop a pollutant management system. Therefore, direct treatment of eutrophic water is often required for the restoration of closed water bodies, which must be superior technically and economically.

So-called alum sludge is water treatment works sludge containing an aluminium coagulant such as polyaluminium chloride (PAC). The total amount of alum sludge produced in the world is enormous, estimated to be 10 thousand dry solids (DS) tons per day in 1997 and to be steadily increasing (Dharmappa et al. 1997). In Japan, 280 thousand DS tons are wasted annually, corresponding to 2% of the industrial wastes. In recent years, successful application of alum sludge to constructed wetlands has been reported by Zhao et al. (2015) at University College Dublin (Babatunde & Zhao 2007). Also, among several low-cost and engineered materials, alum sludge performed best in terms of selective phosphorus removal from surface water and minimum undesirable secondary changes in water chemistry (Boyer et al. 2011).

For waste wood, there are various sources and generation forms, such as thinnings, forest residues and wastes from lumbering and construction/demolition. In Japan, the amount of generation is huge, 15 million DS tons per year. Since approximately 40% of waste wood and alum sludge are not recycled in Japan, more active recycling is required for constructing a sustainable society (Ministry of the Environment 2007). As reviewed by Schipper et al. (2010), denitrifying bioreactors utilizing carbon substrates from wood can be a low-cost and simple approach for reducing nitrate loads to receiving waters.

In this study, alum sludge and wood were investigated as economical filtration media for the direct treatment of eutrophic lake water, simply because they are wasted in large quantities and can be reused economically. Also, intended was the recovery of a valuable nutrient, phosphorus, from alum sludge.
MATERIALS AND METHODS

Continuous experiment

A continuous experiment was performed with the two laboratory-scale processes as shown in Figure 1. Process 1 consisted of Column 1 and Column 2 in series, and Process 2 of Column 3. All columns were made of clear acrylic resin, and had a diameter of 7.5 cm, height of 32 cm and effective volume of 0.5 L. Column 1 contained 52.5 g dry weight (DW) of wood as the filtration media, which were disposable wooden chopsticks made from white birch, and cut into several centimetres length. Column 2 and 3 contained about 340 g DW (0.4 L) of alum sludge with 0.60–2.36 mm particle size. The alum sludge was collected from a water treatment plant in Fukui City, Japan (PAC is used as the coagulant in the plant). The bottom of all columns were covered with 0.1 L of gravel (>4.7 mm).

The lake water was collected twice (on the 1st and 57th day) from a eutrophic lake, Kitagata Lake in Awara City, Japan, and, before use, was transferred to the 40 L influent tank agitated at approximately 60 rpm in shadow. Using a peristaltic pump, the flow rate to the columns was controlled at the filtration velocity of 0.45 m/d in Run 1 and 0.91 m/d in Run 2 (HRT of 6 and 3 hours, respectively). The water quality of influent and effluent was analysed weekly, and the composition of alum sludge before and after the experiment.

Leaching of dissolved organics from wood

Leaching of dissolved organics from the wood was examined in a batch mode. Forty-nine grams DW of wood was introduced to 1.0 L of 0.01 mM phosphate buffer solution in an Erlenmeyer flask, and rotated at 100 rpm at room temperature. The concentration of soluble organics in the solution was measured as total organic carbon (TOC) in appropriate time intervals. The phosphate buffer was used to maintain a neutral pH range of 6.9–7.4.

Phosphate consumption in lake water

This batch experiment was conducted to confirm phosphate consumption by phytoplankton. Without any addition of chemicals such as a coagulant, 10 L of lake water was placed in a plastic container agitated slowly at 20 rpm. The phosphate concentration in the lake water was monitored for 2 days. An identical experiment was also conducted with an artificial phosphate solution to eliminate the influence of phytoplankton.

Adsorption isotherm of alum sludge

Adsorption equilibrium between the alum sludge and phosphate was investigated by a batch test using Erlenmeyer flasks. Different amounts of alum sludge (96, 144, 152,
The alum sludge was quantified for total carbon (T-C), T-N, phosphate (as P₂O₅), potassium (as K₂O), aluminium (as Al₂O₃) and silicon (as SiO₂). P₂O₅, K₂O, Al₂O₃ and SiO₂ were analysed according to Methods for Fertilizer Analysis (National Institute for Agro-Environmental Sciences 1992). A CN analyser (MT-700, Yanaco, Kyoto, Japan) was used for the T-C and T-N analysis.

RESULTS AND DISCUSSION

Continuous experiment

Run 1 and Run 2 were operated for 49 days each. The major results are plotted in Figure 2 and summarized in Table 1. For suspended solids (SS) removal, both processes performed well, showing an average removal efficiency of about 98%. Consequently, the effluents were mostly composed of soluble species, such as nitrate and phosphate ions.

Soluble TOC (S-TOC) concentrations were similar between the influent and effluent. The resultant S-TOC removal efficiency was 15–14%. Thus, it can be said that excessive dissolution of organic matter from wood was not observed in this study.

For T-N, in Process 1, the average removal efficiency reached 64–72%, and most of T-N was removed in Column 1, where biological denitrification can take place using organics supplied from the wood. According to the review by Schipper et al. (2010), denitrification wood beds have proven successful at nitrate removal rates of 2–22 mg N/L-d, and other important factors are temperature and influent nitrate concentration. In this continuous study, the nitrate load to Column 1 was 6.1 mg N/L-d and 7.4 mg N/L-d in Run 1 and Run 2, respectively. Therefore, receiving nitrate loads within the proper range, Column 1 removed nitrate moderately with an average efficiency of 60–73% (66–78% as T-N). By contrast, in Process 2, consisting of only alum sludge filtration, the average nitrate removal efficiency was much lower, 1–12% (18–19% as T-N). Process 2 appears to rely on the trap of particulate nitrogen in the filter.

In both processes, T-P in effluent was reduced quite low, 0.01–0.02 mg/L, corresponding to an average removal efficiency of 88–92%. Thus, the alum sludge

Phosphorus extraction from alum sludge

After the continuous experiment was terminated, recovery of phosphorus from the alum sludge used was attempted following the alkaline extraction method adapted by Gifu City, Japan, for wastewater sludge incineration ash (Nakagawa 2011). In a glass beaker, 10 g wet weight of alum sludge was added to 100 mL of 1 mol/L NaOH (L/S ratio of 10), and mixed by a magnetic stirrer at 300 rpm and 70 °C for 1 hour. The solutions were filtered with 0.45 μm membrane filters for subsequent phosphate analysis. This procedure was repeated with the used NaOH solution to explore the possibility of successive use of the alkaline solution.

Analytical procedures

Most of the analyses were performed in accordance with Wastewater Examination Methods (JSWA 1997). In the continuous experiment, the soluble solution of the influent and effluent was prepared through filtration (No. 5C, Advantec, Japan). PO₄³⁻-P was measured by the ascorbic acid method, using a spectrophotometer (DR/4000U, Hach, San Bernardino, CA, USA) with appropriate dilution. NO₃⁻-N was analysed with an ion chromatograph (DX-120, Dionex, Sunnyvale, CA, USA). For the analysis of total nitrogen (T-N) and total phosphorus (T-P), samples were digested by the alkaline persulfate digestion method (4500E-N C; APHA/AWWA/WEF 2000). The samples for total carbon (T-C) and total phosphorus (T-P), were prepared from a standard phosphate solution (1,000 mg P/L of KH₂PO₄ dissolved in water) (Wako-Junyaku, Hiratsuka, Japan). PO₃ with a TOC Analyzer (TOC-Vesh, Shimadzu, Kyoyto, Japan). The pH of 7.5

193, 216 and 272 mg) and 100 mL of about 1 mg/L phosphate solution were added to the flasks, adjusted to the pH of 7.5 ± 0.1, and rotated at 100 rpm at room temperature. Dilute hydrochloric acid and sodium hydroxide solutions were used for the pH adjustment. After 5 days, the solutions were filtered with 0.45 μm membrane filters, and then subjected to phosphate analysis. The phosphate solution used was prepared from a standard phosphate solution (1,000 mg P/L of KH₂PO₄ dissolved in water) (Wako-Junyaku, Hiratsuka, Japan).
was shown to have a superior ability to adsorb phosphate at the filtration velocities applied. Interestingly, a significant amount of phosphorus was removed even with the wood media in Column 1, achieving an average T-P removal efficiency of 67–85%. This is primarily attributable to the particulate phosphorus removal by the filter. In addition, phosphate seems to be incorporated by micro-organisms, such as denitrifying bacteria and phytoplankton. The possible consumption by phytoplankton is demonstrated later.

The phosphorus consumption for the growth of denitrifying bacteria can be estimated stoichiometrically. Assuming glucose as the electron donor and the solids retention time of 20 days, the overall biological denitrification reaction is written as follows (Rittmann & McCarty 2000):

\[
\text{NO}_3^- + 0.321\text{C}_6\text{H}_{12}\text{O}_6 + 1.002\text{H}^+ \\
= 0.117\text{C}_2\text{H}_7\text{O}_2\text{N} + 1.341\text{CO}_2 + 0.443\text{N}_2 + 2.018\text{H}_2\text{O}
\]

(1)

Based on the above stoichiometric relation and bacterial composition of C\text{C}_6\text{H}_{12}\text{O}_6\text{N}_{0.1}, the mass ratio of P required for synthesis against \text{NO}_3^-\text{N} denitrified is calculated to be 0.0259. In the continuous experiments, this gives the average consumed concentration of 0.029 mg P/L and 0.014 mg P/L from the lake water for Run 1 and Run 2, respectively, corresponding to a T-P removal efficiency of 9.0–14.4%. Obviously, the consumption by denitrifying bacteria can constitute part of the phosphorus removal mechanisms.

Owing to the use of PAC in the water treatment plant, aluminium dissolution from alum sludge media into the effluent could be a concern. As the average aluminium concentration in effluent was less than 0.02 mg/L (average removal efficiency of 97–99%) for both processes, the aluminium dissolution from the alum sludge was negligible. This result is consistent with Babatunde et al. (2011), who concluded that the effluent aluminium concentration is well below the Irish effluent standard of 0.2 mg/L except for the initial starting period.
Denitrification bioreactors with wood have been generally applied to wastewater and wastewater effluent, in which nitrogen and organic concentrations are much higher. To our knowledge, few studies have examined phosphorus removal mechanisms in wood beds in detail. The wood beds seem to be unstable at high filtration velocities, as stated above. Therefore, alum sludge filtration may be necessary to polish the effluent, when strict phosphorus removal is required.

Also, Zhao et al. (2013) have mainly dealt with constructed wetland wastewater treatment with reed. Thus, alum sludge has been rarely applied alone. A report by Boyer et al. (2011) could be the only one, in which surface water with a P concentration of 0.13–0.25 mg/L was treated by a mini-column with alum sludge. T-P and PO$_4^{3-}$-P removal of about 50% or more were achieved at the filtration velocity of 3.7 m/d for 2 days, which might be comparable to the results in this study.

### Table 1 | Summary of the continuous experiment. Average and standard deviation of seven analyses

<table>
<thead>
<tr>
<th>Process 1</th>
<th>Process 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>Col. 1 effluent</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>33.1 ± 5.3</td>
</tr>
<tr>
<td>S-TOC (mg/L)</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>T-N (mg/L)</td>
<td>1.73 ± 0.13</td>
</tr>
<tr>
<td>NO$_3^-$-N (mg/L)</td>
<td>1.53 ± 0.08</td>
</tr>
<tr>
<td>T-P (mg/L)</td>
<td>0.200 ± 0.029</td>
</tr>
<tr>
<td>PO$_4^{3-}$-P (mg/L)</td>
<td>0.048 ± 0.027</td>
</tr>
<tr>
<td>T-Al (mg/L)</td>
<td>1.194 ± 0.200</td>
</tr>
<tr>
<td>pH</td>
<td>7.6 ± 0.2</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>-</td>
</tr>
<tr>
<td>Run 2</td>
<td></td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>26.8 ± 5.3</td>
</tr>
<tr>
<td>S-TOC (mg/L)</td>
<td>1.9 ± 0.4</td>
</tr>
<tr>
<td>T-N (mg/L)</td>
<td>1.18 ± 0.22</td>
</tr>
<tr>
<td>NO$_3^-$-N (mg/L)</td>
<td>0.92 ± 0.25</td>
</tr>
<tr>
<td>T-P (mg/L)</td>
<td>0.159 ± 0.025</td>
</tr>
<tr>
<td>PO$_4^{3-}$-P (mg/L)</td>
<td>0.031 ± 0.018</td>
</tr>
<tr>
<td>T-Al (mg/L)</td>
<td>0.586 ± 0.150</td>
</tr>
<tr>
<td>pH</td>
<td>7.8 ± 0.3</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>-</td>
</tr>
</tbody>
</table>

ORP: oxidation reduction potential.

#### Leaching of dissolved organics from wood

Figure 3 shows a time course of dissolved organic concentration, measured as TOC, which leached from the wood. The solution pH and temperature were 7.0–7.4 °C and 22–24 °C, respectively.
As shown in the figure, organic matter in wood leached quickly within the first few days, and slowly later. As the TOC concentration reached a saturated level, the solution was replaced with a new one at the 20th day. The organic dissolution rate was 1.4 and 1.3 mg C/L-d (0.029 and 0.027 mg C/g DW-d) for the period of the 5th–20th and 20th–35th day, respectively. At these dissolution rates, the denitrification biofilter can be operated for an extraordinarily prolonged period of 50 years theoretically, as the carbon content of wood is approximately 50% (Japan Wood Research Society 2010). There is evidence that full-scale denitrification bioreactors for wastewater effluent have continued for 7–15 years with nitrate removal of 50% or more (Schipper et al. 2013). For wastewater treatment, Yamashita et al. (2014) have confirmed that stable operation lasted for more than 4 years.

**Adsorption isotherm of alum sludge**

Adsorption equilibrium between the alum sludge and phosphate was obtained applying the Langmuir equation, which gives the saturated adsorption capacity of the adsorbent. The Langmuir plot is shown in Figure 4, and the Langmuir constants calculated are shown below ($R^2 = 0.96$)

$$q = \frac{q_{\text{max}}KC}{1 + KC} = 0.89 \cdot 41C/(1 + 41C) \quad (2)$$

where $q$ is the amount of phosphate adsorbed per unit weight of alum sludge (mg/g DW), $C$ is the equilibrium phosphate concentration (mg/L), $q_{\text{max}}$ is the maximum amount of phosphate adsorbed per unit weight of alum sludge (mg/g DW) and $K$ is a constant. The solution pH was maintained at 7.4–7.6, and the room temperature at 23–24 °C.

This phosphate adsorption capacity, 0.89 mg/g DW, is much lower than synthetic adsorbents, for example, approximately 100 mg/g for ceramic with ion exchange capacity (Shimizu 2011) and layered double hydroxides (Tsuji et al. 2012). However, it is comparable to that of Irish alum sludge, approximately 1–2 mg/g at pH 7–8 (Yang et al. 2006). Yang et al. (2006) also observed that ligand exchange is the dominating mechanism for phosphate removal by alum sludge, and that its adsorption capacity is strongly dependent upon the solution pH.

If we assume 0.003 mg/L PO$_4^{3-}$-P in the effluent, the amount of PO$_4^{3-}$-P adsorbed is calculated to be 0.10 mg/g DW. As 340 g DW of alum sludge per column was used in the continuous study, each column is estimated to have a potential of adsorbing 34 mg PO$_4^{3-}$-P. The amount of PO$_4^{3-}$-P actually removed during the whole period was approximately 1.5 mg and 10 mg for Column 2 and 3, respectively. Accordingly, it is inferred that the alum sludge used in the continuous study was under saturation with respect to phosphate. Thus, the installation of alum sludge filtration depends on the situation, as described before.

**Phosphate consumption in lake water**

The time course of phosphate concentration in the lake water is shown in Figure 5. In this batch experiment, the pH was slightly increased from 7.6 to 7.9 at the room temperature of 24–25 °C. The lake water originally contained 31 mg/L of SS and 97 μg/L of chlorophyll-a, and the light intensity was somewhere between 100 and 300 lux in the daytime and 0 lux at night-time.
The phosphate concentration in the lake water was decreased from 0.13 to about 0.03 mg/L after 1 day and to about 0.01 mg/L after 2 days. On the other hand, the phosphate concentration of the artificial solution did not change much. This result implies that phytoplankton took up phosphate from the lake water. Therefore, in Column 1 of the continuous experiment, where the light conditions were identical to this batch test, part of the phosphate removal appears to be due to their biological activity. This further implies that activating phytoplankton may be a promising way to achieve concomitant removal of nitrogen and phosphorus only with wood filtration. Furthermore, since denitrifying bacteria require phosphorus as a nutrient, as calculated above, there must be competition between denitrifying bacteria and phytoplankton for phosphorus in the wood filter.

Phosphorus extraction from alum sludge

Table 2 shows the composition of the alum sludge before and after the continuous experiment. As shown in the table, the content of phosphorus and other elements stayed relatively constant during the experiment.

The results of the alkaline extraction are shown in Table 3. Sixty-five to sixty-nine percent of phosphorus in the alum sludge was extracted for the first use of NaOH solution, verifying that this extraction method is useful. The phosphorus thus extracted can be easily recovered as calcium phosphate ultimately. The study by Babatunde & Zhao (2009) indicates that aluminium and iron phosphate forms are amenable to the alkaline extraction, while the phosphorus left after the alkaline extraction is in the form of calcium phosphate, magnesium phosphate or inactive phosphorus.

Table 2 | Composition of alum sludge. Unit: %DW

<table>
<thead>
<tr>
<th></th>
<th>Before use</th>
<th>Col. 2</th>
<th>Col. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-C</td>
<td>5.67</td>
<td>6.06</td>
<td>6.68</td>
</tr>
<tr>
<td>T-N</td>
<td>0.56</td>
<td>0.66</td>
<td>0.65</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.56</td>
<td>0.60</td>
<td>0.61</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.46</td>
<td>0.48</td>
<td>0.44</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>23.4</td>
<td>23.6</td>
<td>24.8</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>49.8</td>
<td>53.4</td>
<td>47.4</td>
</tr>
</tbody>
</table>

Table 3 | Phosphorus extraction from the alum sludge by the alkaline method

<table>
<thead>
<tr>
<th></th>
<th>Before use</th>
<th>Col. 2</th>
<th>Col. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st use of NaOH soln</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;-P (mg/L)</td>
<td>148</td>
<td>151</td>
<td>163</td>
</tr>
<tr>
<td>P recovery (%)</td>
<td>66.3</td>
<td>65.2</td>
<td>68.9</td>
</tr>
<tr>
<td>2nd use of NaOH soln</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;-P (mg/L)</td>
<td>–</td>
<td>299</td>
<td>307</td>
</tr>
<tr>
<td>P recovery (%)</td>
<td>–</td>
<td>64.0</td>
<td>65.0</td>
</tr>
</tbody>
</table>

The total amount of T-P removed from the lake water, however, was only 9.0 and 45.7 mg in the continuous experiment for Column 2 and Column 3, respectively, compared to 831 mg P per column in the alum sludge before use. Thus, phosphorus extracted in this way was mostly that originally contained in the alum sludge. It is, therefore, recommended to operate the alum sludge column up to its saturation level.

The extraction efficiency for the second use of NaOH solution was almost the same as that for the first use, as shown in Table 3. Therefore, repeated use of the NaOH solution could be possible, which is advantageous economically. A possible problem associated with this extraction method is browning of the solution, probably due to the reaction between NaOH and organic matter in the alum sludge, and thus the colour intensity is increased more when the solution is used repeatedly.

CONCLUSIONS

In this study, two filtration processes using alum sludge and/or wood as the media were applied to the direct treatment of lake water at the filtration velocity of 0.45 and 0.91 m/d. The conclusions reached are as follows:

1. In both processes, SS removal was excellent with a removal efficiency of about 98%.
2. T-N removal efficiency was higher (64–72%) in Process 1 than in Process 2 (18–19%). Biological denitrification proceeds using organic substrates dissolved from wood in Process 1, while particulate nitrogen is mostly captured by filtration in Process 2.
3. In both processes, about 90% of T-P removal was achieved. In addition to trapping particulate phosphorus in the filter, phosphate was removed by the adsorption to alum sludge and biological uptake by denitrifying bacteria and phytoplankton.

4. The dissolution of organics and aluminium, respectively, from the wood and alum sludge, was not significant in the effluent.

5. Sixty-five to sixty-nine percent of phosphorus in the alum sludge can be extracted by applying the alkaline extraction method. Repeated use of the alkaline solution is possible, making this method economically attractive.

Based on these findings, the combination of alum sludge and wood filtration enables the concomitant removal of nitrogen and phosphorus, and thus is very effective for directly purifying eutrophic lake water and reusing the wastes beneficially. In addition, recoverability of phosphorus is another advantage of applying alum sludge.

REFERENCES


Babatunde, A. O., Kumar, J. L. G. & Zhao, Y. Q. 2011 Constructed wetlands using aluminium-based drinking water treatment sludge as P-removing substrate: should aluminium release be a concern? J. Environ. Monit. 13, 1775–1783.


Zhao, X. H., Zhao, Y. Q. & Kearney, P. 2013 Phosphorus recovery as AlPO₄ from beneficially reused aluminium sludge arising from water treatment. Environ. Technol. 34, 263–268.

First received 5 December 2014; accepted in revised form 6 February 2015. Available online 21 March 2015