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Development of alum sludge-based constructed wetland: An innovative and cost-effective system for wastewater treatment

Y.Q. ZHAO¹*, A.O. BABATUNDE¹, X.H. ZHAO¹ and W.C. LI¹

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Abstract

This paper describes (in a summarised manner) a research attempt to integrate the dewatered alum sludge, a residual by-product of drinking water treatment process, into a constructed wetland (CW) system for the purpose of enhancing the wastewater treatment performance, thus developing a so-called alum sludge-based constructed wetland system. A multi-dimensional research project including the batch tests of phosphorus (P) adsorption onto alum sludge followed by the model CWs trials of single and multi-stage CWs, has been conducted since 2004. It has been successfully demonstrated that the alum sludge-based CW is capable of enhanced and simultaneous removal of P and organic matter (in terms of BOD₅ and COD), particularly from medium and high strength wastewater. The sludge cakes act as the carrier for developing biofilm for organics removal and also serve as adsorbent to enhance P immobilization. Batch P-adsorption tests revealed that the alum sludge tested possesses excellent P-adsorption ability of 14.3 mg-P/g.sludge (in dry solids) at pH 7.0 with the adsorption favored at lower pH. The results obtained in a 4-stage treatment wetland system suggest that high removal efficiencies of 90.4% for COD, 88.0% for BOD₅, 90.6% for SS, 76.5%...
for TN and 91.9% for $\text{PO}_4^{3-}$-P under hydraulic loading of $0.36\text{m}^3/\text{m}^2\cdot\text{d}$ can be achieved. The field demonstration study of this pioneering development is now underway.

**Keywords:** Alum sludge; constructed wetland; reuse; substrate; wastewater treatment

**Introduction**

In line with sustainable wastewater treatment technologies which are environmentally friendly, easy to operate, less energy-intensive and cost-effective, constructed wetland (CW) has been recognised as a “green technology” that falls into the category of sustainable wastewater treatment technologies. Although CWs have been shown to be very efficient in removing suspended solids and organics (in terms of BOD$_5$ and COD), their performance has been inconsistent and often low as regards nutrient removal. There is even more concern when they are used to treat medium to high strength wastewaters. [1] Consequently, prominent research goals of CWs are to continually seek specialized substrates with conducive physico-chemical properties to improve nutrient removal (especially P) and to improve its design and operation, so as to facilitate enhanced oxygen availability in order to achieve a higher degree of organics removal and nitrification. [2]

In the past five years, series of projects of different scales have been conducted at the University College Dublin, Ireland, towards developing the novel alum sludge-based CW system for wastewater treatment. Alum sludge refers to a resultant residual sludge, which is derived from potable water treatment process that employs aluminium sulphate as coagulant to reduce the levels of suspended particles, colour and organic matters in source water. Although the most prevalent final disposal of the dewatered alum sludge is as a “waste” to landfill worldwide, the reuse of the alum sludge is now attracting international attention. [3-5] The idea of reuse dewatered alum sludge as
main substrate in CW lies in its specific characteristics of abundant Al content and easy, local and huge availability.

The main steps of the development towards the alum sludge-based CW system for P-rich wastewater treatment are shown in Fig. 1. In the first step, emphasis was placed on assessing the feasibility of the use of the dewatered alum sludge as an adsorbent and its capacity for P adsorption. According to [6,7], the alum sludge was extensively characterized and the P adsorption behaviour coupled with the P adsorption capacity of the dewatered alum sludge was examined. [8,9] Thereafter, the optimal configuration of the proposed alum sludge based system, which will give the best operational, hydraulic and treatment performance was determined using four different model reed beds systems, configured with different proportions of the alum sludge and fed with a high P-rich agricultural wastewater. Emphasis during this phase of the study was placed on isolating the magnitude of the overall pollutant removal in the different model systems. The potential for bed clogging and possible release of substances/elements from the alum sludge into the treated wastewater upon passage through the system was also examined.

Upon the determination of the optimal configuration of the reed bed system, the model CWs (in single column form) with dewatered alum sludge as main substrate were operated for short term [10] and long term trial over two years. [11] Thereafter a multi-stage CW system was designed and continuously operated to treat an agricultural wastewater with strong organic and nutrient pollutants under high organic loading. The trial of the multi-stage system will continue to focus on addressing the lifespan of the system as well as the final reuse of the alum sludge as resourceful material when it becomes fully saturated in the reed bed treatment system.

[Fig. 1 here]
The main objective of this paper is to present the overall technical progression towards the development of the alum sludge-based CW system. Therefore, the overall view of such the development, rather than the detailed results and analysis, is given in this paper.

**Experimental approaches**

**Dewatered alum sludge and wastewater**

Dewatered alum sludge cake (with moisture content of 72-75%) was obtained from a local Water Treatment Plant outside Dublin, Ireland where aluminium sulphate is used for flocculating reservoir water. After collection, the sludge was air-dried, ground and sieved to prepare the sludge for batch P-adsorption test and model CW trials. The aluminium content (expressed as Al₂O₃) in the sludge tested by ICP-AES (inductively coupled plasma-atomic emission spectrometry) was 24.7-46.3%, depending on the seasonal dosage of aluminium sulphate. Artificial P solutions were used in batch tests while raw wastewater collected from an animal farm with about 2000 livestock units including sheep, pigs, cattle and horses was used for the model alum sludge-based CW trial. The typical concentration of such animal farm wastewater (after settlement) was 322-510 mg/L (SS), 720-1523 mg/L (COD), 540-850 mg/L (BOD₅), 210-350 mg/L (TN), 147-275 mg-PO₄³⁻/L (P) and 6.7-7.6 (pH). During the experiment, the wastewater was diluted with tap water if necessary and used as influent to the CW system.

**Batch P-adsorption tests**

P-adsorption was studied by a series of batch adsorption tests using a standard Stuart Orbital Shaker (SSL 1, Bibby Sterilin Ltd.). Different weight of prepared dewatered alum sludge was poured into plastic bottles which were filled with artificial P solution using 3 kinds of P-containing chemicals including orthophosphate (KH₂PO₄), polyphosphate (BDH(NaPO₃)₆) and organic phosphate...
(C<sub>10</sub>H<sub>14</sub>N<sub>5</sub>O<sub>7</sub>P · H<sub>2</sub>O). Adsorption tests were conducted under varying pH of the P solution, initial P concentration and agitating time. The maximum adsorption capacity (mg/g) was obtained by fitting of experimental data with Langmuir isotherm.\textsuperscript{[7]}

**Optimal configuration trial**

Four identical Pyrex columns of 1000 mm in height and 95 mm in diameter were designed using different configurations (not shown in schematic diagram). The columns were filled with prepared alum sludge and overlain with pea gravel in different proportions ranging from 0 to 60%. In other words, the proportion of the alum sludge in the four columns was 100%, 80%, 60% and 40%. A real agricultural farm wastewater contained in a single feed tank was equally pumped to each of the columns and the treatment efficiency for the pollutants including SS, P and COD was monitored for 25 weeks under hydraulic loading rate ranged between 1.23-1.86 m³/m².d.

**The model CWs**

The schematic diagrams of a single model CW and a multi-stage CW system used in the study are jointly shown in Fig. 2. The model CWs were made of Perspex columns. The single model CW is 1000 mm in height and 145 mm in diameter. The model CW was filled with dewatered alum sludge up to 350 mm in depth with a bottom layer of gravel (100mm depth) which serves as support material at the bottom of the model CW. The multi-stage CW system consists of four identical single CW. Each stage was 900 mm in height and 95 mm in diameter. The prepared alum sludge was filled into the CWs up to a depth of 550 mm and with a support base of 100mm-depth of gravel. Common reeds, *Phragmites australis*, were planted on each of the CWs. Both the single and 4-stage model CWs were operated using a novel operational strategy referred to as ‘tidal flow’ in which the ‘tide’, i.e. the rhythmical filling and draining of the bed medium, was generated by peristaltic pump controlled by timer.\textsuperscript{[2,12]} The hydraulic loadings of the single model CW and the 4-
stage CW system were 0.50 m$^3$/m$^2$·d and 0.36 m$^3$/m$^2$·d, respectively.

[Fig. 2 here]

**Sampling and analysis**

Procedure of the batch tests and sampling were described elsewhere. [7,9] Samples of batch P-adsorption tests were subjected for P analysis using a HACH DR/2400 Colorimeter (CAMLAB Ltd, UK) according to its manual. During the optimal configuration trial and CWs experiments of single model CW and multi-stage CW system, samples of influent and effluent from the CW (or each stage of the CWs) were collected and analyzed for SS, COD, BOD$_5$, TN, P, and pH. A PHM62 standard pH meter was used for the pH analysis. BOD$_5$ was determined using a BODTrack apparatus (CAMLAB Ltd., UK). The COD value was read directly on the HACH DR/2400 Colorimeter after the sample was digested at 150°C for 2 hrs in a HACH COD digester according to the dichromate method. The SS value was read directly with the HACH DR/2400 Colorimeter. PO$_4^{3-}$ value was also measured with HACH DR/2400 Colorimeter after reaction with Molybdovanadate. TN was determined according to persulfate digestion method and the value was read after 5 min of reaction with TN Reagent C in a 25 mL standard glass cell.

**Results**

The maximum P adsorption capacity ($Q_0$) determined via Langmuir isotherm from the batch tests when the source P of KH$_2$PO$_4$ was used is listed in Table 1, which shows that the dewatered alum sludge has a high P immobilization ability and can be used as an adsorbent for P removal. However, the adsorption ability is significantly favoured at lower pH.
The typical results of the optimal configuration trial are given in Table 2. It can be seen that the alum sludge can be employed as substrate to serve as filter medium for SS removal and as biofilm carrier for COD reduction although the COD removal efficiency is quite low due to the high hydraulic loading of 1.2-1.9 m³/m².d. More significantly, the enhanced P immobilization proves the advantage of such use in the column. The inclusion of pea gravel at the infiltrative surface of the columns did not prove to have any significant beneficial advantage. In addition, all the four columns exhibited clogging tendencies irrespective of the substrate configuration. Interestingly, removal of SS in gravel-containing columns seemed lower than that of pure alum sludge column (see Table 2). However, there is lack in further SS removal measurement regarding clogging investigation in this study.

The results of the single model CW (refer to Fig. 2) tests are summarised in Table 3. It can be seen that while the removal of organics in the model CW increased gradually with time during the testing period, the removal of P was very high in the initial stages, and in particular, it remained high throughout the experimental period. It is interesting to note from Table 3 that as the experiment progressed and the system further stabilized, the removal of organics was considerably significant in the system, and even at higher loadings. It can be suggested that the initial removal of the carbonaceous substrates is through filtration while improved removal was obtained gradually through aerobic degradation as the system stabilized and matured.

The results of the 4-stage CW system (refer to Fig. 2) operated for 110 days using an animal farm
wastewater are illustrated in Fig. 3. An average removal percentage of 90% for COD and 88% for 
$\text{BOD}_5$ was achieved. These results are very similar with those obtained from a reed bed system 
using soil and gravel as main substrate. [13] The performance of the system on SS, P and TN removal 
showed that significant removal of P was achieved in the system and 92% of the influent $\text{PO}_4^{3-}$-P 
was consistently removed. This is believed to be attributable to the adsorption of P onto the alum 
sludge due to its strong affinity. [6] The average removal of TN and SS is 76% and 91% 
respectively, as shown in Fig. 3. A higher TN removal efficiency appears to be observed in the later 
stage of the trial. If this is the case, the promoted removal may be due to the progressively matured 
microbial activities and the reed uptake. High SS removal in the system is believed to be due to the 
filtration and the physical trapping of the particles by the alum sludge, which serves as the filter 
medium in the system.

[Fig. 3 here]

**Discussion**

Studies on several potential CWs substrates including minerals and rocks, soils, marine sediments, 
industrial by-products and man-made products show their P-removal capacity to vary from 0.025 to 
32mg-P/g. [14] In comparison, the dewatered alum sludge used herein can be seen to have a 
significant and comparable P adsorption capacity (Table 1). A variation of the adsorption maxima 
with pH could possibly be attributed to the change of surface potential of the adsorbent particles 
(alum sludge) and the combined effects of phosphate speciation and pH both on the adsorbent 
particles, and in solution.

After identifying the adsorption capacity of dewatered alum sludge, an attempt to develop the alum 
sludge-based CW was made. It should be pointed out that such development is hinged on the basis
that: (1) alum sludge is a locally, easily and hugely available material; (2) reuse of such water
industrial by-product falls into the theme of environmental sustainability which encourages “reduce,
reuse and recycle”; (3) P removal is an universal environmental problem and the reuse of such
sludge will enhance the removal of P from P-rich wastewater. Research of different phases in the
development of such novel CW provided convincing data to demonstrate that the dewatered alum
sludge is a promising material, which can be reused as a substrate in CW for wastewater treatment.
Removal of COD and BOD₅ can be achieved at about the same level as in soil and gravel-based
CW system. [13] This is a good demonstration of the dewatered alum sludge being a carrier for
biofilm development. It provided a surface for biofilm attachment which served to enhance
microbial activity in the CW. More importantly, P removal can be significantly enhanced (Fig. 3),
and this provides evidence to show that the dewatered alum sludge as a novel adsorbent and
substrate in CW can considerably improve the P-immobilization capacity. Due to the fact that alum
sludge is currently treated as a waste for landfill, the reuse of such sludge in CW will be reasonably
collected as a cost-effective solution in CW development.

It is interesting to note that the lifespan of the alum sludge in CW regarding its saturation for P
adsorption was estimated according to the P-adsorption capacity and the operation condition of the
CW system. [11] In case of domestic wastewater treatment using alum sludge-based CW, the lifespan
of the alum sludge can be 9–40 years [11] when the total P discharge per person per day of 2.3g of P
was estimated and CW area of 5 m² per person was proposed. [15] Even in the case of P-rich animal
farm wastewater treatment tested in this study, the lifespan of the dewatered alum sludge is
estimated as 2.5–3.7 years. [11] Moreover, in most cases of the practical use of CW system, a multi-
stage treatment system is usually applied. Therefore, the lifespan is reasonably expected to be
longer. This is also an ongoing investigation in the multi-stage model CW system. In addition,
studies on the P desorption and recovery from the saturated alum sludge after use was conducted.
Several kinds of acids (HCl, HNO$_3$, and H$_2$SO$_4$) and bases (NaOH and KOH) were tested to extract P from saturated alum sludge, which was used as media in CW. The results, which are given in Table 4, show that either acid or base is efficient for P extraction and the efficiency relies mainly on the concentrations of H$^+$/OH$^-$, and not on the type of acid or base. Under 0.1M H$^+$/OH$^-$, around 90% of P can be extracted from the used alum sludge by acids, but only 65-66% by bases within 1 hour. By considering the convenience and safety of extraction operation, H$_2$SO$_4$ seems to be the best reagent for such the P extraction.

It should be pointed out that during the testing period, especially in the 4-stage model CW system trial, no obvious and serious bed clogging occurred. However, regarding the practical operation in real situation of long term point of view, possible clogging behaviour and measures to reduce/mitigate clogging should be investigated, since clogging is the most serious problem in practice. This reflects the need for large scale and long term demonstration study of such novel CW treatment system development, which is currently underway.

**Conclusions**

It is expected that this pioneering investigation on the possible application of dewatered alum sludge as main substrate in a constructed wetland system treating P-rich wastewater would serve as a primer for eventual field application. The results have demonstrated the promise of such novel application of the “waste” alum sludge. Batch P-adsorption tests revealed that the alum sludge tested possesses excellent P-adsorption ability with the adsorption favored at lower pH. The results obtained in the 4-stage treatment wetland system suggest that high removal efficiencies of 90.4% for COD, 88.0% for BOD$_5$, 90.6% for SS, 76.5% for TN and 91.9% for PO$_4^{3-}$-P under hydraulic loading of 0.36m$^3$/m$^2$·d can be achieved. However, long term operation should be conducted for
further investigation of such innovative approach, especially the engineering aspect of the large scale application. Notwithstanding, the development so far supports the proposition that the potential reuse of dewatered alum sludge as a substrate in constructed wetland system can be a promising solution to transfer alum sludge as a “waste” to a useful raw material, in developing a cost-effective treatment wetland system.

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References


[7] Zhao, Y.Q.; Razali, M.; Babatunde, A.O.; Yang, Y.; Bruen, M. Reuse of Aluminium-based water treatment sludge to immobilize a wide range of phosphorus contamination: Equilibrium study with different isotherm models, Separation Science and Technology, 2007, 42, 2705-2721.


## Tables

### Table 1 Maximum P-adsorption capacity (with sludge particle size <0.063mm, tested by KH$_2$PO$_4$ under initial P of 102 mg/L and equilibrium time of 48 hrs)

<table>
<thead>
<tr>
<th>pH</th>
<th>4.3</th>
<th>6.0</th>
<th>7.0</th>
<th>8.5</th>
<th>9.0</th>
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<tr>
<td>$Q_0$ (mg-P/g.sludge)</td>
<td>22.4</td>
<td>18.3</td>
<td>14.3</td>
<td>1.1</td>
<td>0.9</td>
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### Table 2 Typical results of optimal configuration trial

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<th>Parameter</th>
<th>1# (100% sludge)</th>
<th>2# (80% sludge)</th>
<th>3# (60% sludge)</th>
<th>4# (40% sludge)</th>
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<tr>
<td><strong>P (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>89.3</td>
<td>88.9</td>
<td>70.2</td>
<td>60.6</td>
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<tr>
<td><strong>SS (%)</strong></td>
<td>64.6</td>
<td>63.0</td>
<td>45.5</td>
<td>49.4</td>
</tr>
<tr>
<td><strong>COD (%)</strong></td>
<td>30.5</td>
<td>36.2</td>
<td>27.7</td>
<td>30.9</td>
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### Table 3 Results (mean±SD) of the single model CW trial

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<tr>
<th>Parameter</th>
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<th>13-16</th>
<th>17-20</th>
<th>21-28</th>
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<td><strong>BOD$_5$ Loading (g/m$^2$.d)</strong></td>
<td>35.8±8.5</td>
<td>50.0±6.7</td>
<td>57.5±10</td>
<td>114.8±15</td>
<td>111.7±13</td>
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<tr>
<td><strong>Removal (%)</strong></td>
<td>63.3±16</td>
<td>71.7±5.2</td>
<td>75.9±1.4</td>
<td>80.3±7.1</td>
<td>82.3±3.5</td>
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<tr>
<td><strong>COD Loading (g/m$^2$.d)</strong></td>
<td>66.7±21</td>
<td>77.1±12</td>
<td>99.4±13</td>
<td>187.6±25</td>
<td>183.6±11</td>
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<tr>
<td><strong>Removal (%)</strong></td>
<td>50.2±9.1</td>
<td>75.1±3.8</td>
<td>78.0±3.1</td>
<td>84.4±2.8</td>
<td>85.5±2.1</td>
</tr>
<tr>
<td><strong>P Loading (g/m$^2$.d)</strong></td>
<td>3.3±1.3</td>
<td>4.7±0.9</td>
<td>6.0±1.3</td>
<td>8.4±1.3</td>
<td>10.3±1.3</td>
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<tr>
<td><strong>Removal (%)</strong></td>
<td>88.9±2.9</td>
<td>90.2±0.5</td>
<td>90.3±1.3</td>
<td>89.0±1.0</td>
<td>88.1±0.5</td>
</tr>
<tr>
<td><strong>SS Loading (g/m$^2$.d)</strong></td>
<td>23.9±2.9</td>
<td>36±1.3</td>
<td>38.1±1.7</td>
<td>75.6±5.5</td>
<td>84.6±3.3</td>
</tr>
<tr>
<td><strong>Removal (%)</strong></td>
<td>76.4±20</td>
<td>79.8±14</td>
<td>83±9.2</td>
<td>86±12.7</td>
<td>91.7±3.2</td>
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### Table 4 P release efficiency by different acid or base with different H$^+$/OH$^-$ concentrations

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<tr>
<th>Acid/Base</th>
<th>HCl</th>
<th>HNO$_3$</th>
<th>H$_2$SO$_4$</th>
<th>NaOH</th>
<th>KOH</th>
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<tr>
<td>0.01 M</td>
<td>4.2</td>
<td>4.2</td>
<td>4.8</td>
<td>16.3</td>
<td>17.8</td>
</tr>
<tr>
<td>0.03 M</td>
<td>41.2</td>
<td>42.0</td>
<td>37.5</td>
<td>46.0</td>
<td>52.5</td>
</tr>
<tr>
<td>0.05 M</td>
<td>75.0</td>
<td>72.2</td>
<td>72.3</td>
<td>60.8</td>
<td>61.2</td>
</tr>
<tr>
<td>0.075 M</td>
<td>85.8</td>
<td>89.8</td>
<td>88.5</td>
<td>65.5</td>
<td>63.3</td>
</tr>
<tr>
<td>0.1 M</td>
<td>90.7</td>
<td>91.0</td>
<td>88.5</td>
<td>66.1</td>
<td>65.3</td>
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Unit: %
Figure captions

Fig. 1 Road map of the development of the alum sludge-based CW

Fig. 2 The schematic of the experimental CWs systems

Fig. 3 Summarized performance of the 4-stage CW system

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Fig. 2
Fig. 3