

1 **Alum sludge-based constructed wetland system for enhanced removal of P**  
2 **and OM from wastewater: Concept, design and performance analysis**  
3

4 **A.O. Babatunde, Y.Q. Zhao\* and X.H. Zhao**

5 Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering,  
6 Newstead Building, University College Dublin, Belfield, Dublin 4, Ireland  
7

---

8 \*Corresponding author: Tel: +353-1-7163215, Fax: +353-1-7163297

9 E-mail: yaqian.zhao@ucd.ie  
10

11 **Abstract**

12 The concept, design and performance analysis of a four-stage novel constructed wetland  
13 system (CWs) capable of enhanced and simultaneous removal of phosphorus (P) and organic  
14 matter (OM) from wastewaters is described. Alum sludge, a largely available by-product of  
15 drinking water facilities using aluminium salts as coagulant was used as the media. Under a  
16 hydraulic loading rate of 1.27 m<sup>3</sup>/m<sup>2</sup>.d and a range of organic loading rate of 279.4–774.7 g-  
17 BOD<sub>5</sub>/m<sup>2</sup>.d and 361.1–1028.7 g-COD/m<sup>2</sup>.d, average removal efficiencies (mean ± SD) of  
18 90.6 ± 7.5% for BOD<sub>5</sub> and 71.8 ± 10.2% for COD were achieved, respectively. P removal was  
19 exceptional with average removal efficiency of 97.6 ± 1.9% achieved for soluble reactive P at  
20 a mean influent concentration of 21.0 ± 2.9 mg/l. Overall, the system holds great promise as a  
21 novel CWs for simultaneous removal of P and OM, and at the same time, it transforms alum  
22 sludge from a waste into a useful material.  
23

24 **Keywords:** Alum sludge, constructed wetlands, phosphorus, tidal flow, self organizing maps  
25  
26  
27  
28

## 29 **1. INTRODUCTION**

30 Constructed wetland systems (CWs) are wastewater treatment systems that encompass a  
31 plurality of treatment modules which are akin to processes occurring in natural wetlands.  
32 They have the advantage of low cost and lower energy consumption and they have been  
33 applied globally to treat various types of wastewaters (Babatunde et al. 2008; Park, 2009).  
34 Generally, their performance is good in terms of removal of suspended solids (SS) and  
35 organic matter (OM), but inconsistent and often low for nutrient reduction (particularly  
36 phosphorus (P)). Consequently, CWs research has been geared towards improving P removal  
37 using novel materials with high P adsorption capacity (Johansson Westholm, 2006,  
38 Babatunde et al., 2009). Our previous study has demonstrated the feasibility of using  
39 dewatered alum sludge cakes as main substrate in a single-stage model CWs to enhance P  
40 removal (Zhao et al., 2009). The current study is concerned with the design and performance  
41 of a multistage model of the CWs employing dewatered alum sludge as major substrate. The  
42 system has two unique features in its design: (i) Use of dewatered alum sludge cakes as main  
43 substrate to enhance P removal and for biofilm attachment. Alum sludge is the most widely  
44 generated water treatment residual worldwide, and is mostly landfilled since it is regarded as  
45 a by-product of little known reuse value (Babatunde and Zhao, 2007). However, the chemical  
46 composition of alum sludge, particularly its abundant aluminium gives it a highly reactive  
47 surface and a strong affinity for P immobilization (Makris et al., 2005; Makris and O'Connor,  
48 2007; Babatunde et al., 2009), and it can also serve as biofilm carrier (Zhao et al., 2009). Its  
49 use as a CWs medium has the potential of improving wastewater treatment and also  
50 transforming alum sludge from 'waste' into useful material; (ii) Use of multiple CWs stages  
51 operated with tidal flow strategy to better simulate the practical use of this novel CWs system.  
52 Tidal flow operation is a batch wise, fill-and-draw type operation (Green et al., 1997, 1998;  
53 Sun et al., 1999). By operating multiple CWs stages in series using the tidal flow mode, the  
54 capacity for oxygen transfer is increased leading to a greater organic matter mineralization.

## 55 2. MATERIALS AND METHODS

56 The CWs consist of 4 interlinked stages set up in the laboratory using Pyrex columns with  
57 internal diameter of 9.5cm. Each stage was filled up to a depth of 50cm with air-dried  
58 dewatered alum sludge cakes which were collected from a local water treatment plant (Zhao  
59 et al., 2009). After collection, the sludge was air-dried, ground and sieved to have a  $d_{10}$  and  
60  $d_{60}$  of 0.5 mm and 1.8 mm, respectively (Babatunde et al., 2009). Each stage had 10cm of 6-  
61 10mm gravel at the base to serve as support and young *Phragmites australis* was planted on  
62 top of each stage. The CWs was operated using the tidal flow strategy which was carried out  
63 in cycles with a hydraulic loading rate (HLR) of  $1.27 \text{ m}^3/\text{m}^2\cdot\text{d}$ . Each cycle consist of 1 hour of  
64 wastewater contact and 3 hours of stage resting. The influent wastewater had a concentration  
65 of  $392.7 \pm 95.6 \text{ mg/l}$  ( $\text{BOD}_5$ ),  $579.8 \pm 142.0 \text{ mg/l}$  (COD),  $45.2 \pm 6.2 \text{ mg-P/l}$  (RP (reactive P),  
66 which refers to P determination carried out on unfiltered samples),  $21.0 \pm 2.9 \text{ mg-P/l}$  (SRP  
67 (soluble reactive P), which refers to P determination carried out on filtered samples),  
68  $218 \pm 97.8 \text{ mg/l}$  (SS) and  $7.81 \pm 0.25$  (pH). Influent and effluent samples from the system  
69 were collected periodically and analyzed for  $\text{BOD}_5$ , COD, SS, turbidity,  $\text{P-PO}_4^{3-}$  (both RP and  
70 SRP), pH,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$  and TN according to standard methods (APHA, 1998).  
71 Self organizing maps (SOM) technique (Aguado et al., 2008) was used to mine data on  $\text{BOD}_5$ ,  
72 COD, RP and SRP. Dissolved oxygen profile was also monitored in the headspace of stages 1  
73 and 2 of the CWs in order to examine the tidal flow concept. The theoretical amount of  
74 oxygen drawn into each stage of the system in each tidal cycle was also determined. The  
75 determination is however a simple and basic approach meant as a guide only as removal of  
76 OM is quite a complicated and extremely biological process which can also be influenced by  
77 OM adsorption, roots aeration, nitrification/denitrification, or anoxic removal of OM.

78

## 79 3. RESULTS AND DISCUSSION

### 80 **3.1 General treatment performance**

81 Fig. 1 shows the removal trend for organics (BOD<sub>5</sub> and COD) and P (RP and SRP). The  
82 system achieved higher removal efficiencies for BOD<sub>5</sub> than for COD. Average removal  
83 efficiencies of  $90.6 \pm 7.5\%$  and  $71.8 \pm 10.2\%$  for BOD<sub>5</sub> and COD respectively, were achieved.  
84 This is quite possible as the ratio of BOD<sub>5</sub> concentration to COD concentration ( $C_{\text{BOD}}/C_{\text{COD}}$ )  
85 ranged between 0.59–0.91, which indicates high biodegradability. However, the average  
86  $C_{\text{BOD}}/C_{\text{COD}}$  in the effluent exiting the system was 0.23 indicating low biodegradability. A  
87 conceptual model to describe the biodegradation process has been developed (Babatunde et  
88 al., 2007). Comparatively, the system achieved a comparable performance with other similar  
89 systems such as those reported by Sun et al. (1999); Cerezo et al. (2001) and Zhao et al.  
90 (2004a) even though it had a relatively smaller footprint and higher loading. P removal in the  
91 system was exceptional. In particular, the system proved very effective for the removal of  
92 soluble reactive phosphorus (SRP) and showed superior P removal performance when  
93 compared to similar performances in literature such as Sun et al. (1999); Cerezo et al. (2001)  
94 and Zhao et al. (2004b).

95 **[INSERT FIG 1 HERE]**

96 The SOM results are shown in Fig. 2. From the mapping, it can be determined that the BOD-  
97 in component is mostly negatively correlated with the BOD-out component. This indicates  
98 that even with higher influent BOD values, the effluent BOD values are still low and further  
99 suggests that in the CWs under study, it will be possible to obtain higher performance and  
100 achieve low effluent BOD<sub>5</sub> values even at high influent values. For the COD mapping, the  
101 lower part of the COD-in map only had some slight positive correlation with high COD-out  
102 values. This is because that the COD in the final effluent from the system was relatively  
103 higher than the BOD<sub>5</sub> values. As it has been discussed previously, average BOD<sub>5</sub>/COD value  
104 of final effluent was 0.23, indicating that most of the organics in the wastewater have been

105 degraded in the CWs. For RP and SRP, the local average values for both RP-out and SRP-out  
106 were very low irrespective of the influent levels. The exceptional ability of the system to  
107 achieve very low effluent P concentrations irrespective of the influent P concentration can be  
108 attributed to the P adsorption ability of the alum sludge (Yang et al., 2006a, b; Babatunde et  
109 al., 2009).

110 **[INSERT FIG. 2 HERE]**  
111

112 The removal fraction in each stage of the system is shown in Table 1. High removal fractions  
113 were obtained in the first stage of the system irrespective of the pollutant and this reflects its  
114 key role. The individual contribution of the subsequent stages to overall removal ranged from  
115 6-23% (BOD<sub>5</sub>) and 7-16% (COD). Nonetheless, the reduction obtained in stage 4 had some  
116 contribution to the overall reduction. However, there was no significant P removal beyond the  
117 first stage. P removal will be significantly performed in subsequent stages when the first stage  
118 becomes saturated. The removal of SS and the reduction of turbidity followed the same trend  
119 as the removal of organics with the highest and most significant reduction obtained in the first  
120 stage, while although there were further reductions in the subsequent stages, their relative  
121 contribution were less significant. It is however worthy to note that effluent ponding on the  
122 surface was experienced but this was resolved by bed resting.

123  
124 There was a slight reduction in the overall removal of total nitrogen (TN), with an average  
125 overall removal of 22.8% obtained. However, NH<sub>4</sub>-N was reasonably removed with an  
126 average overall removal of 73.2% obtained. Furthermore, there was an increase in the level of  
127 NO<sub>3</sub>-N which suggests nitrification as the nitrifying bacteria converted NH<sub>4</sub>-N in the influent  
128 to NO<sub>2</sub>-N and further to NO<sub>3</sub>-N.

129 **[INSERT TABLE 1 HERE]**  
130

### 131 **3.2 Dissolved oxygen profiling**

132 The results (data not shown) of the oxygen profiling show that the percentage decrease in  
133 oxygen was higher in stage 1 than in stage 2, indicating that more dissolved oxygen is utilised  
134 in the first stage than in the second stage. Furthermore, based on the trend in the percentage  
135 oxygen concentration, the following suggestions can be made. Prior to pumping of  
136 wastewater, the headspaces in the stages were equilibrated with the atmosphere and therefore  
137 saturated with air. During and after the pumping which is also the period of contact of the  
138 system with wastewater, there was a little drop in the oxygen concentration in the system but  
139 this could have been caused by air-drift, instrument error, or it is possible that actual  
140 microbial-degradation is taking place. The change noticed during the pump out stage is  
141 probably due to suction effect of the draining wastewater. However, the most significant drop  
142 in concentration was when the stages were at rest and the decrease was calculated to be  
143 ca.16% and 10% in the first and second stages respectively. A 16% change would imply that  
144 40.32 mg/l of oxygen was utilized by the microorganisms in the first stage and up to 80.64  
145 mg/l of BOD<sub>5</sub> can be removed in the first stage. Consequently, 10% - 25% of the oxygen  
146 input is available as dissolved oxygen for microbial oxidation and this puts the oxygen  
147 transfer efficiency of the system under study at about 5.3-13.3 g-O<sub>2</sub>/m<sup>2</sup>. cycle.

148

### 149 **CONCLUSIONS**

150 A novel multi-stage constructed wetland system (CWs) using alum sludge as substrate was  
151 operated to enhance concurrent removal of phosphorus (P) and organic matter from  
152 wastewater. The system achieved high removal efficiencies for BOD<sub>5</sub> (90.6%), COD (71.8%),  
153 reactive P (80%) and soluble reactive P (89%). The concept holds great promise as an  
154 attractive option for achieving high and concurrent removal of P and OM from wastewaters in  
155 CWs and in addition, it borders on sustainability by reusing a by-product as its main substrate.

156 **Acknowledgements**

157 Authors gratefully acknowledge the Irish Environmental Protection Agency for providing  
158 financial assistance for this study through the Environmental Technologies Scheme (project  
159 No. 2005-ET-MS-38-M3). The University College Dublin Lyons Estate Farm in particular,  
160 Dr Edward Jordan and Mr Michael Hegarthy are sincerely thanked for their cooperation.

161

162 **References**

- 163 Aguado, D., Montoya, T., Borrás, L., Seco, A., Ferrer, J., 2008. Using SOM and PCA for  
164 analysing and interpreting data from a P-removal SBR. *Engineering Applications of*  
165 *Artificial Intelligence*. 21, 919-930.
- 166 APHA-AWWA-WEF, 1998. Standard methods for the examination of water and wastewater.  
167 20<sup>th</sup>. ed. American Public health association, Washington, DC
- 168 Babatunde, A.O., Zhao, Y.Q., 2007. Constructive approaches towards water treatment works  
169 sludge management: A review of beneficial reuses. *Critical Reviews in Environmental*  
170 *Science and Technology*. 37(2), 129-164.
- 171 Babatunde, A.O., Zhao, Y.Q., Yang, Y., Kearney, P., 2007. From 'fills' to filter: Insights into  
172 the reuse of dewatered alum sludge as a filter media in a constructed wetland. *Journal of*  
173 *Residuals Science & Technology*, 4 (3), 147-152
- 174 Babatunde, A.O., Zhao, Y.Q., O'Neill, M., O'Sullivan, B., 2008. Constructed wetlands for  
175 environmental pollution control: A review of developments, research and practice in  
176 Ireland. *Environment International*. 34(1), 116-126
- 177 Babatunde, A.O., Zhao, Y.Q., Burke, A.M., Morris, M.A., Hanrahan, J.P., 2009.  
178 Characterization of aluminium-based water treatment residual for potential phosphorus  
179 removal in engineered wetlands. *Environmental Pollution*. 157, 2830–2836
- 180 Cerezo, R.G., Suarez, M.L., Vidal-Abarca, M.R., 2001. The performance of a multi-stage  
181 system of constructed wetlands for urban wastewater treatment in a semiarid region of SE  
182 Spain. *Ecol. Eng.*, 16(4), 501-517.
- 183 Green, M., Friedler, E., Ruskol, Y., Safrai, I., 1997. Investigation of alternative method for  
184 nitrification in constructed wetlands. *Water Sci. Technol.* 35(5), 63-70.
- 185 Green, M., Friedler, E., Safrai, I., 1998. Enhancing nitrification in vertical flow constructed  
186 wetland utilizing a passive air pump. *Water Res.* 32(12), 3513-3520

- 187 Johansson Westholm, L., 2006. Substrates for phosphorus removal-Potential benefits for on-  
188 site wastewater treatment? *Water Res.* 40 (1), 23–36.
- 189 Makris, K.C., Harris, W.G., O'Connor, G.A., El-Shall, H., 2005. Long-term phosphorus  
190 effects on evolving physicochemical properties of iron and aluminum hydroxides. *Coll. &*  
191 *Interface Sci.* 287(2), 552-560
- 192 Makris, K.C., O'Connor, G.A., 2007. Beneficial utilization of drinking-water treatment  
193 residuals as contaminant-mitigating agents. *Developments in Environmental Sciences.* 5,  
194 609-635
- 195 Park, W.H., 2009. Integrated constructed wetland systems employing alum sludge and oyster  
196 shells as filter media for P removal. *Ecol. Eng.*, 35, 1275-1282
- 197 Sun, G., Gray, K.R., Biddlestone, A.J., Cooper, D.J., 1999. Treatment of agricultural  
198 wastewater in a combined tidal flow downflow reed bed system. *Water Sci. Technol.*  
199 40(3), 139-146.
- 200 Yang, Y., Tomlinson, D., Kennedy, S., Zhao, Y.Q., 2006a. Dewatered alum sludge: A  
201 potential adsorbent for phosphorus removal. *Water Sci. Technol.* 54(5), 207-213
- 202 Yang, Y., Zhao, Y.Q., Babatunde, A.O., Wang, L., Ren, Y.X., Han, Y., 2006b. Characteristics  
203 and mechanisms of phosphate adsorption on dewatered alum sludge. *Sep. Pur. Technol.*  
204 51, 193-200.
- 205 Zhao, Y.Q., Sun, G., Allen, S.J. 2004a. Anti-sized reed bed system for animal wastewater  
206 treatment: a comparative study. *Wat Research.* 38(12), 2907-2917.
- 207 Zhao, Y.Q., Sun, G., Allen, S.J., 2004b. Purification capacity of a highly loaded laboratory  
208 scale tidal flow reed bed system with effluent recirculation. *Sci Tot. Env.* 330, 1-8.
- 209 Zhao, Y.Q., Zhao, XH., Babatunde, A.O. 2009. Use of dewatered alum sludge as main  
210 substrate in treatment reed bed receiving agricultural wastewater: Long-term trial.  
211 *Bioresour. Technol.* 100(2), 644-648.

212  
213  
214  
215  
216  
217  
218  
219  
220  
221  
222  
223

Table 1 Overall and inter-stage treatment performance in the system

Parameter	Influent	Stage 1	Stage 2	Stage 3	Stage 4	% removal
BOD <sub>5</sub>	392.7	184.1 <b>(53)</b>	93.7 <b>(23)</b>	60.4 <b>(9)</b>	37.1 <b>(6)</b>	90.6
COD	579.8	353.7 <b>(39)</b>	260.7 <b>(16)</b>	200.1 <b>(11)</b>	158.1 <b>(7)</b>	71.8
SRP	21	2.3 <b>(89)</b>	1.2 <b>(5)</b>	0.86 <b>(2)</b>	0.47 <b>(2)</b>	97.6
RP	45.3	8.9 <b>(80)</b>	5.7 <b>(7)</b>	3.7 <b>(4)</b>	3.0 <b>(2)</b>	93.3
SS	218	72.9 <b>(67)</b>	39.8 <b>(15)</b>	29.2 <b>(5)</b>	19.3 <b>(5)</b>	89.3
Turbidity	127.7	46.4 <b>(64)</b>	26.5 <b>(16)</b>	18.6 <b>(6)</b>	14.3 <b>(3)</b>	86.7
TN	142.5	133.8 <b>(64)</b>	125.6 <b>(6)</b>	120 <b>(4)</b>	110 <b>(7)</b>	22.8
NH <sub>4</sub> -N	132.9	87.1 <b>(35)</b>	46.8 <b>(30)</b>	40.2 <b>(5)</b>	35.6 <b>(4)</b>	73.2
NO <sub>2</sub> -N	0.75	0.23	0.13	0.06	0.15	—
NO <sub>3</sub> -N	3.6	9	27.2	9.5	25	—
pH	7.81	7.0	6.82	6.82	6.81	—

224 All parameter values are in mg/l, except pH (no unit) and turbidity which is in NTU. All P values are in mg-P/l. Bold values  
 225 in bracket refer to the amount of removal in percentage obtained in each respective stage, relative to the initial concentration  
 226 in the wastewater and expressed as a percentage  
 227  
 228  
 229  
 230  
 231  
 232  
 233  
 234  
 235  
 236  
 237  
 238  
 239  
 240  
 241  
 242  
 243  
 244  
 245  
 246  
 247

248 **Figure captions:**

249

250 Figure 1. Trend of pollutant removal efficiencies in the novel constructed wetland system

251

252 Figure 2. Abstract visualization of the relationship between influent and effluent values of  
253 BOD<sub>5</sub>, COD, RP and SRP in the constructed wetland system using self organizing  
254 maps

255

256

257

258

259

260

261

262

263

264

265

266

267

268

269

270

271

272

273

274

275

276

277

278

279

280

281

282

283

284

285

286

287

288

289

290

291

292

293

294

295

296

297

298

299

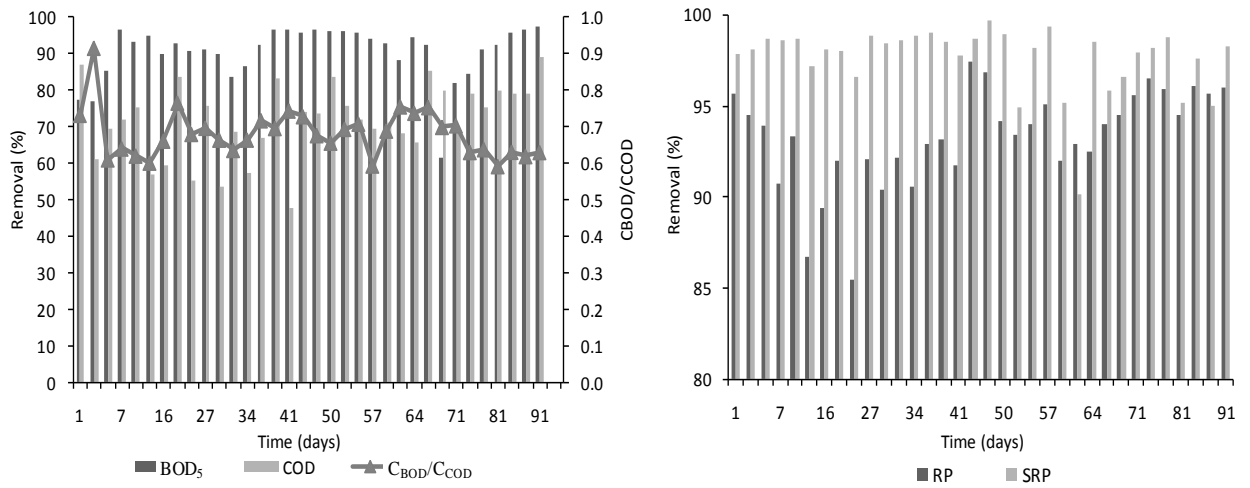


Fig. 1

300  
 301  
 302  
 303  
 304  
 305  
 306  
 307  
 308  
 309  
 310  
 311  
 312  
 313  
 314

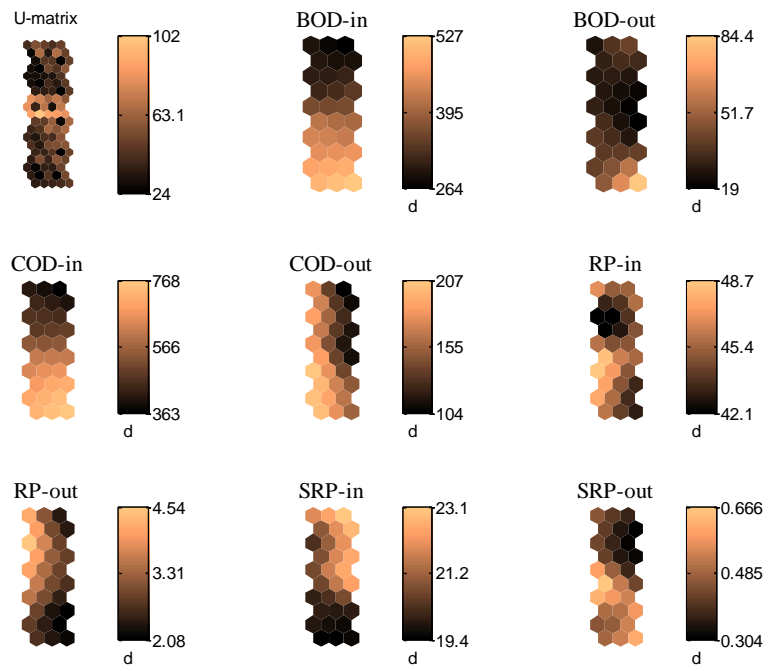


Fig. 2

315  
316  
317