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Phosphorus removal in laboratory-scale unvegetated vertical subsurface flow constructed wetland systems using alum sludge as main substrate

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Abstract This research has two eventual goals: (1) To optimize performance of subsurface constructed wetlands for removal of phosphorus (P) (2) To demonstrate that dewatered alum sludge (a by-product), can be reused as a constructed wetland substrate. To achieve these, alum sludge from a water treatment plant was characterized and used as main substrate in four experimental vertical sub-surface flow constructed wetland systems treating dairy farm wastewater. Results show that the alum sludge has suitable hydraulic characteristics (uniformity coefficient = 3.6) for use as a substrate, and in the batch studies, up to 48.6mg-P was removed by 1g of the alum sludge at a P concentration of 360mg-P/l and a dosage of 5g/l. Results from the experimental systems highlight the significant P removal ability of the alum sludge. However, the inclusion of pea gravel at the infiltrative surface of some of the systems had a negative effect on the P removal performance. Sequential P-fractionation results show that there was no significant increase in the easily extractable P, but for total P, there was significant increase, although this was found to decrease with depth. This study shows that the novel use of dewatered alum sludge can bring about high P removal in vertical subsurface flow constructed wetland systems.

Keywords Alum sludge; constructed wetlands; water treatment residual; phosphorus

INTRODUCTION

Vertical sub-surface flow constructed wetland systems (VSSFCW) with intermittent loading represents one of the latest generation of subsurface flow constructed wetlands worldwide. Due to their enhanced aeration efficiency, these systems are capable of high rate of organics removal and they are also able to achieve low effluent ammonia-nitrogen concentration. Design for dimensioning VSSFCW commonly vary between 1 and 2 m²/pe and up to 5m²/pe (Cooper, 1999), but these design guide are for organics removal in the strictest sense. So far, the biggest operational problems of these systems have been substrate clogging and substrate phosphorus (P) saturation. Therefore, to operate VSSFCW at typical high loading rates without clogging and with a sustained high nutrient (particularly phosphorus, (P)) removal capacity remains a prominent research and development goal in constructed wetland technology.

Consequently, the quest for suitable media for VSSFCW have implied the selection/use of materials, which have good hydraulic characteristics, consistent and sustained high P removal capacity and is/are cheap and locally available. In addition, it is usually desirable that upon P saturation, such substrates should be amenable to being used as a slow P-release fertilizer. The early VSSFCW used gravel as the substrate, being a material with a seemingly suitable hydraulic conductivity to be used as a constructed wetland substrate. However, P removal in these systems is poor (ca. 30%), as is the case in typical constructed wetland systems (Vymazal, 2007). It is now known that P removal in constructed wetlands is limited by the capacity of the media to adsorb, bind or precipitate the incoming P. Therefore, numerous researches have focused on screening materials and/or industrial by-products for their P-removing ability and suitability as constructed

wetland substrate. Lena (2006) gave a comprehensive review of such materials cited in literature and they include minerals and rocks, soils, marine sediments, industrial by-products and man-made products. Another prospective by-product which can be used to optimize P removal in VSSFCW is alum sludge. Alum sludge refers to the residual product obtained as a result of the water treatment processes including coagulation, flocculation, clarification and filtration, followed by conditioning and dewatering, in plants using aluminium sulphate as the primary coagulant. The disposal of the dewatered alum sludge cakes is highly regulated worldwide, and there are on-going efforts at its beneficial reuse (Babatunde and Zhao, 2007). However, noting that the daily global production of dewatered alum sludge cakes is in excess of 10,000 t/d, more research is needed to discover more novel ways of reusing this material. On one hand, there is a huge potential in utilizing the dewatered alum sludge cakes as a substrate for optimizing P removal in VSSFCW, being that it consists mainly of amorphous aluminium. Past works have identified the P removing ability of alum sludge (Zhao et al., 2007), but no research has been carried out to extend this ability into a wastewater treatment system. This paper presents part of a new initiative aimed at optimizing P removal and the overall treatment performance in VSSFCW. Unvegetated VSSFCW were constructed in the laboratory using Pyrex columns and the results from the systems, designed and developed using the dewatered alum sludge cakes as the main substrate are presented and discussed.

MATERIALS AND METHODS

Dewatered alum sludge cake was obtained from a 400MI/d water treatment plant located on the shores of the Poulaphuca reservoir, Co. Kildare, Ireland. The sludge cake is an $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, organic polymer residue. The water content, bulk density and residual pH were determined according to standard procedures. Analysis of particle size distribution was carried out on the dewatered sludge cakes to calculate the values of d_{10} and d_{60} and determine the uniformity coefficient (UC). Surface characteristics of the sludge were examined using a scanning electron microscope (SEM) and EDX-microanalysis. Detailed characterization, including quantitative elemental composition of the alum sludge were carried out and these have been reported (Babatunde, 2007; Babatunde et al., 2009). The alum sludge was air dried, ground and sieved, and used as main substrate in four unvegetated experimental VSSFCW designated as 1, 2, 3, and 4 as shown in Fig. 1. The experimental VSSFCW were constructed using Pyrex tubes and the substrates were filled to a depth of 0.6m which is the same as that typically used in field-scale VSSFCW. The characteristics and configuration of the individual unit is summarized in Table 1. Each unit had 10-cm of gravel layer at the bottom to act as support. The VSSFCW were all fed with diluted dairy farm wastewater from the same source at a mean hydraulic loading rate (HLR) of $1.7\text{m}^3/\text{m}^2 \cdot \text{d}$ across the four systems. Inflow into each of the systems was designed to reach a preset point just beneath the surface of the alum sludge bed. Influent and effluent samples were collected periodically and analyzed for P on a HACH DR-2400 spectrophotometer according to the standard methods for the examination of water and wastewater (1998).

At the end of the experiments, substrate samples were taken from selected points in the VSSFCW and sequential P-extraction was conducted. Sequential fractionation of the P-forms in the filter media can provide an opportunity to understand which forms of ions in the filter media sorbed P and what type of transfer processes occurred between these ions and P (Zhu et al., 1997). Only the extraction results of total P and KCl extractable P for the system 1 are presented and discussed here, due to the enormous amount of data. Total P was determined by ashing samples at 550°C for 4 h and extracted with 6 M HCl (Forbes et al., 2005). The extract was then analysed for Total P following sulfuric acid-potassium persulfate digestion, using an autoclave. KCl extractable P was measured at a ratio of 1:2.5 in a 0.01 M KCl solution. KCl extractable P is considered the most available (labile) pool of P (Makris and O'Connor, 2007). After the necessary treatments, all the forms of P were determined colorimetrically as described above.

RESULTS AND DISCUSSION

Characterization

The characteristics, physical structure and gradation of alum sludge depend largely on the source water and the pertinent treatment plant operations. The alum sludge used herein has a residual pH of 6.0 and an aluminium concentration of 42.7mg/g-Al (Babatunde, 2007). The pH is within the typical pH range of 5.10 to 8.00 as reported by Dayton and Basta (2001) and this may be attributed to hydrolysis effect of the alum sludge in aqueous solution. The sludge has a bulk density of 1.3g/cm³ and an electrical conductivity of 0.14 dS/m. Based on the electrical conductivity value of the sludge, it can be considered non-saline. This implies that there should be no concerns about the water uptake of plants when the alum sludge is used as a substrate in a constructed wetland system with plants. From the results of the SEM and SEM-EDX shown in Fig. 2, it can be seen that aluminium is a major surface component of the alum sludge. This is further supported by the ICP result which has shown that the alum sludge used in this study has an aluminium content of 42.7mg/g-Al. The aluminum in the sludge is expected to significantly enhance its P-sorption capacity. Fig. 2 (bottom) also shows the SEM image of the sludge cake particle highlighting its porous structure and relating to the potential to adsorb P ions from the aqueous solution.

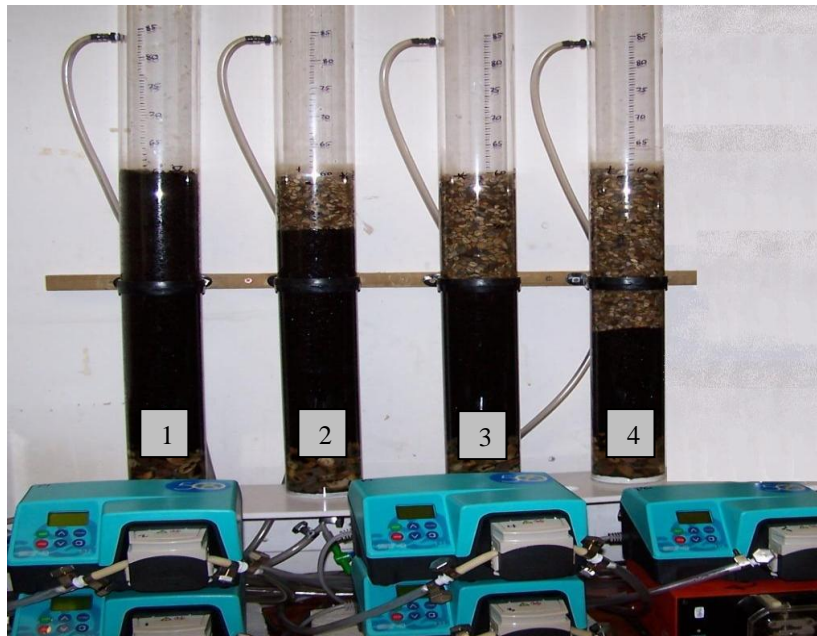


Fig. 1 Unvegetated experimental alum sludge based vertical subsurface flow constructed wetland systems

Table 1 System's characteristics and configuration

Parameter	Constructed wetland system			
	1	2	3	4
Total height (cm)	100	100	100	100
Internal diameter (cm)	9.5	9.5	9.5	9.5
Surface area (cm ²)	70.8	70.8	70.8	70.8
Fill media (Top to bottom)				
Pea gravel (cm)	0	10	20	30
Alum sludge (cm)	50	40	30	20
Fill media (%)				
Pea gravel	0	20	40	60
Alum sludge	100	80	60	40

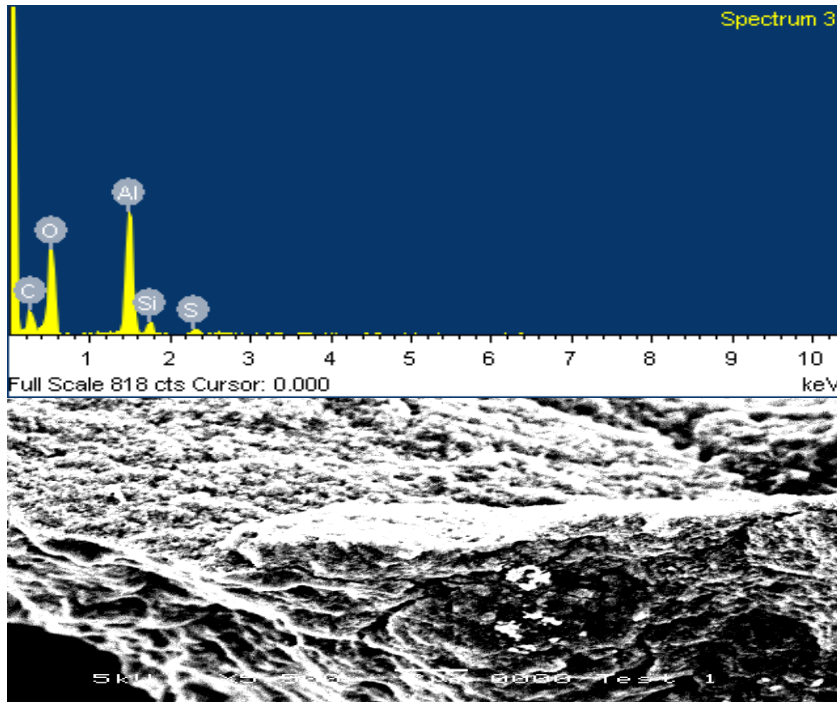


Fig. 2 SEM-EDX (top) and SEM (bottom) of the dewatered alum sludge cakes

Calculated values of d_{10} and d_{60} and the uniformity coefficient (UC) obtained from Fig. 3 are shown in Table 2 and compared with values for other potential VSSFCW substrates presented in literature. The effective size (d_{10}) and the uniformity coefficient are expected to influence the operation time/clogging tendency of constructed wetland substrates. For designing constructed wetlands in Europe, values of $d_{10} > 0.3\text{mm}$ and $d_{60}/d_{10} < 4$ are given as guidelines (Vymazal, 1998; IWA, 2000). The corresponding values for the dewatered alum sludge cakes (listed in Table 2) indicate that the sludge satisfy these guidelines.

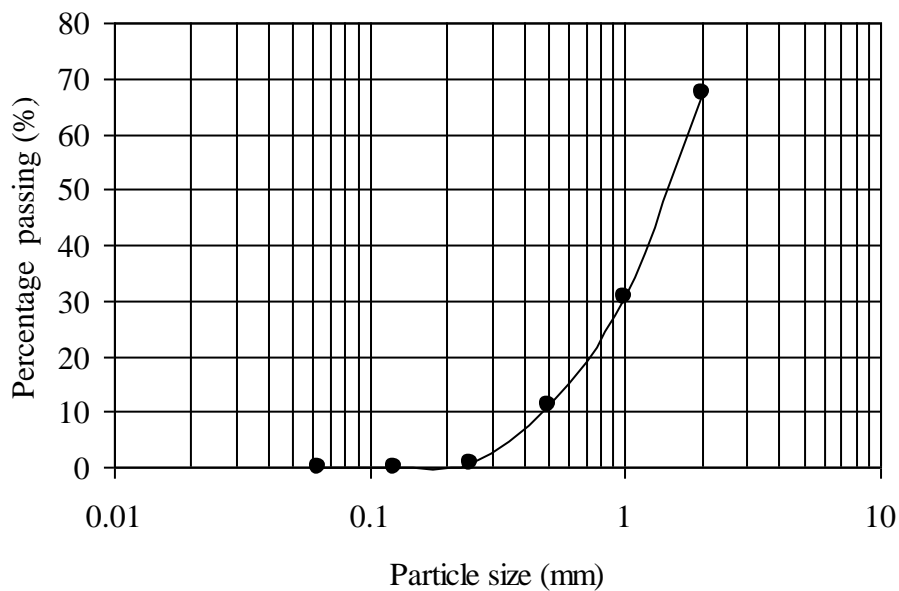


Fig. 3 Analysis of particle size distribution of the dewatered alum sludge

Table 2 Hydraulic characteristic of alum sludge and other materials cited in literature (Additional data from Arias and Brix, 2001)

Material	d_{10} (mm)	d_{60} (mm)	UC (d_{60}/d_{10})
Alum sludge	0.5	1.8	3.6
HACO	0.7	2.3	3.2
Krelde	1.1	3.5	3.2
Filtralite	0.8	3.0	3.8
Soro	0.23	0.7	3.1
Design guide	> 0.3		< 4.0

Phosphorus sorption studies

The initial and final (equilibrium) P concentrations and the calculated P-uptake of the alum sludge used in this study are summarized in Table 3. It can be noted that as the initial P-concentrations of the solutions changed between 0 and 360mg-P/l, the P-uptake of the sludge varied from 0 to 48.6 mg-P/g using an adsorbent dosage of 5g/l and from 0 to 32.8 mg-P/g using an adsorbent dosage of 10g/l. The higher P-uptake were obtained for the higher initial P concentrations. This can be explained by a more efficient utilization of the adsorption capacity of the alum sludge due to a greater driving force initiated by a higher concentration gradient pressure. From the basic reaction of aluminium with P, it can be suggested that as the P concentration in the solution increases, the reactions move to restore equilibrium and the P that is removed from the solution is converted further to insoluble products. These results indicate that alum sludge could be considered as a suitable material for a constructed wetland substrate to significantly enhance P sorption. The maximum P adsorption capacity of alum sludge was determined using the Langmuir adsorption model. A maximum adsorption capacity of 31.9 mg-P g⁻¹ was obtained at pH 4 and this was about three times the value obtained at pH 9 (Babatunde et al., 2009). In comparison with the range of 0.31 mg-P g⁻¹ to 44.2 mg-P g⁻¹ obtained for other similar industrial by-products cited in literature as compiled by Lena (2006), the alum sludge used herein can be seen to have a comparable P adsorption capacity.

Table 3: Results of the P-sorption experiments

		Alum sludge mass									
		5g/l					10g/l				
C_o		0	5	30	120	360	0	5	30	120	360
C_e		0.03	0.07	0.52	14.9	117	0.05	0.03	0.20	4.1	32
q		0	0.99	5.9	21.0	48.6	0	0.5	3.0	11.6	32.8

C_o is the initial P-concentration (mg-P/l), C_e is the final (equilibrium) P-concentration (mg-P/l), q is the P uptake capacity of the alum sludge (mg-P/g of alum sludge).

Phosphorus removal in the experimental VSSFCW

Results of P removal in the experimental VSSFCW are shown in Fig. 4. At the beginning, there was no clear difference in P removal between the systems and all the systems exhibited similar performances, with very low effluent P levels. Although the influent P concentration was relatively higher than those used in other similar studies such as Korkusuz et al. (2007), the effluents from all the systems were comparable. Over time and with further increases in the influent P concentration, clear differences started to emerge as can be observed from the 9th week. Between the 9th and the 18th week, the influent P concentration was increased from 32.9 mg-P/l in the 9th week to 162.1mg-P/l in the 13th week and then further increased to 219.6mg-P/l in the 18th week. During this period, there was only a slight decrease in P removal in systems 1 and 2 from 97- 89% and from 97 – 85% respectively. However, there was significant decrease in P removal for systems 3 and 4 during the same period, from 94 -56% and from 68 – 46% respectively. The two strongly performing systems were 1 and 2. System 1 was however more efficient and it had an average overall removal efficiency of ca. 93.2%. System 4 had the worst performance and it had an average overall removal

efficiency of ca. 67.1%. However, effluent levels from the system 4 had the greatest variation with a standard deviation (S.D) of $\pm 19.5\%$, as compared to the system 1 with a 4.1% S.D. This results shows that the inclusion of pea gravel in the system's design beyond the 0-20% range has negative effect on their P removal performance. Consequently, as the proportion of the pea gravel in the system increased, their P removal performance over a long term period decreased. It should be noted that the pea gravel were initially used at the surface of the systems to sort of improve the hydraulic conductivity of the systems and delay clogging time. Clogging was primarily assessed in the systems by monitoring (any) increase in the height of wastewater in the systems, particularly after each feeding operation and any incidence of ponding on the surface of the system which would suggest clogging of the pore spaces. However, all the systems experienced influent ponding, irrespective of the material at the infiltrative surface. Furthermore, gas physiosorption analysis conducted on surface samples from the systems (analysis not shown) showed that the dewatered alum sludge cake showed less reduction in its mesopores as compared to the gravel, and is probably less susceptible to clogging. Consequently, the use of pea gravel at the infiltrative surface of the system to improve hydraulic conductivity decreases the system's P removing ability and does not serve to significantly improve the clogging time. Surface et al. (1993) reported that although the use of coarse gravel as substrate provided extremely high conductivity in their study, it did not give acceptable treatment performance. However, Sanford et al. (1995) showed that, even gravel experienced decreased hydraulic conductivity and clogging during laboratory simulations. Therefore, it is necessary to determine a 'trade off' point between treatment efficiency and hydraulic conductivity when considering the use of materials for the purpose of enhancing overall constructed wetland performance. The results from this study are consistent with those obtained by Surface et al. (1993) in that the inclusion of the gravel decreased the treatment performance. However, further analysis shows that alum sludge will be less susceptible to clogging as compared to the gravel, under the specific conditions of this study. Thus the inclusions of pea gravel at the infiltrative surface doses not significantly serve to delay the clogging time over the long term. It is therefore recommended that if at all the pea gravel will be included, its inclusion should be limited to the 0-20% range.

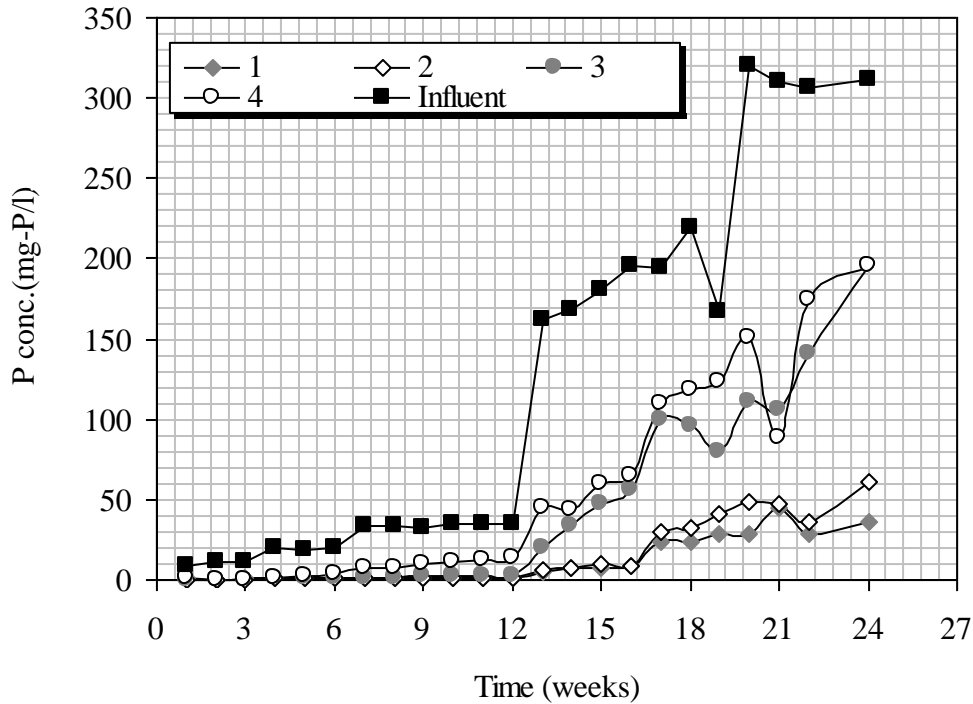


Fig. 4 Trend of P removal in the experimental VSSFCW system showing the influent P and effluent P concentrations from the systems 1, 2,3 and 4 over time

Phosphorus extraction

Results of P extraction shown in Fig. 5 and 6 show that total P content (see Fig 5) was highest in the surface (0-10cm) layer, where the total P content had increased from 0.16mg g^{-1} originally, to 24.8 mg g^{-1} . However, the total P content decreased with depth in the underlying layers of the alum sludge in the system, as can be seen in Fig. 5. This indicates that P from the wastewater was retained in the surface layer of the VSSFCW, when acting as a filter and by the active biomass, which would be more predominant in the surface than in lower layers. Hylander et al. (2006) reported similar trend in P retention using polonite. Noting that at the end of the experiments, the VSSFCW from where the samples were obtained still had an overall P removal efficiency of 93.2%, the dewatered alum sludge cakes can be seen to be capable of being a long-term P sink when used as a VSSFCW substrate. However, results of KCl extractable P shows an irregular pattern (see Fig. 6). While there was an increase in KCl extractable P at the surface layer, from 0.08mg g^{-1} originally to 0.22 mg g^{-1} there was increase/decrease in the 20-30 cm, 30-40 cm and 40-50 cm layers. Overall, the increase in KCl extractable P can be considered marginal. KCl extractable P is considered the most available (labile) pool of P (Elliot et al., 2002, Makris and O'Connor, 2007). Consequently, from this results, it is implied that of the total P sorbed by the alum sludge, only about 0.89% can be easily released, indicating its strong P binding ability and a good potential to be a slow P-release fertilizer upon P saturation. This also suggests the possible P removing and binding mechanism of the alum sludge, but this is outside the scope of this paper.

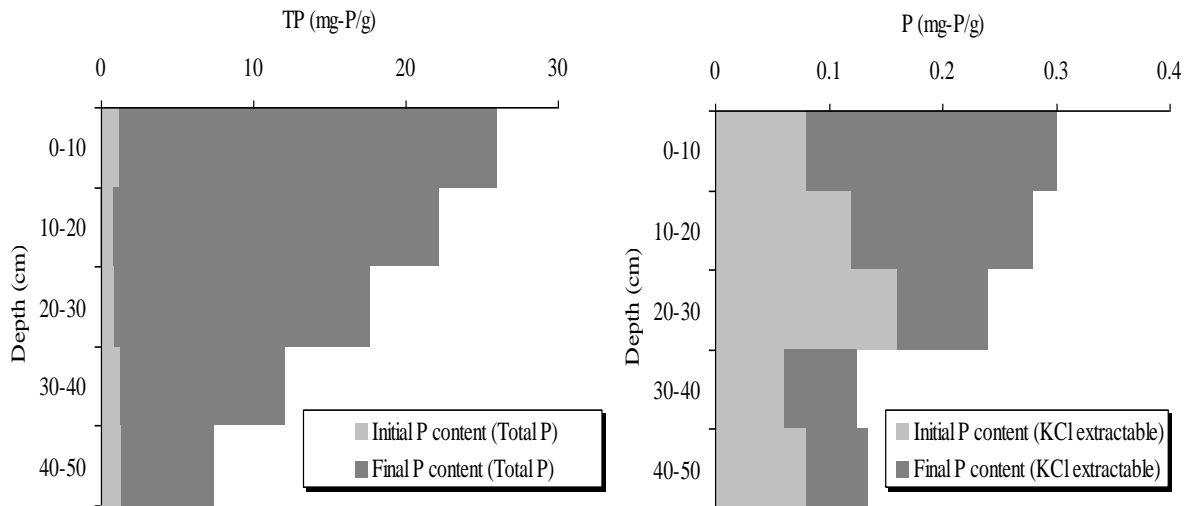


Fig. 5 (left) Initial and final total P content in the used alum sludge cakes and **Fig. 6 (right)** Initial and final P content (KCl extractable) in the used alum sludge cakes. The light shaded areas indicate initial conditions while the dark shaded areas indicate final conditions.

CONCLUSIONS

Dewatered alum sludge cake, a by-product of water treatment process has been shown to be a potential phosphorus removing substrate, for use in subsurface flow constructed wetland systems. The sludge cake has satisfactory grain size distribution with a uniformity coefficient of 3.6, and is shown to be less susceptible to clogging, as compared to gravel when used in a lab-scale system. Results from the lab-scale systems also show that the alum sludge proved beneficial in significantly reducing phosphorus levels in wastewater over a period of 170 days. Overall P removal of 93.2% was achieved in the system without any pea gravel included, whereas, in the system which is composed of 60% gravel, a decrease in P removal was observed with overall P removal of 67.1% obtained. Consequently, it was shown that phosphorus removing ability of the systems decreased with increasing proportion of gravel used. Phosphorus extraction results also show that only about 0.89% of the total P adsorbed by the alum sludge is easily available (labile) as KCl extractable phosphorus. This further indicates its strong phosphorus binding ability and its suitability for use as a slow P-release fertilizer upon P saturation.

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