


Reactive media constructed wetland for phosphorus removal: assessing the opportunity and challenges

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ABSTRACT

Reactive media present an alternative to gravel in constructed wetlands and have the potential to sustainably and efficiently remove phosphorus from wastewater. In this study, a full-scale steel slag wetland has been operated for its whole lifecycle at which 1.39 mg P/g media were retained. During its lifecycle, this wetland met strict consents below 0.5 mg P/L for the first 6 months and was operated for 266 and 353 days before the effluent phosphorus concentration rose above the typical consents of 1 and 2 mg P/L, respectively. A detailed analysis of the system demonstrated that the performance was directly associated with the release of materials from the media into the water which in turn affected other critical parameters such as pH. Further analysis of the media suggested that greater understanding was needed concerning the role of carbonates and in particular calcite if steel slag is to be effectively managed for use on constructed wetlands. Importantly, controlled release of calcium oxide from the media surface is required by managing the concerns of pH and vanadium release.

Key words: constructed wetland, reactive media, P removal, steel slag

HIGHLIGHTS

- First long-term full-scale study of a BOF steel slag media wetland for P removal.
- Phosphorus retention capacity of 1.39 mg P/g media after 782 days of operation.
- Low effluent phosphorus (<2 mg/L) achieved for up to 1 year of operation.
- High phosphorus removal efficiencies were associated with elevated pH (>9).
- Precipitation of calcite, Mg and Fe minerals likely to influence P removal mechanisms.

INTRODUCTION

Wastewater treatment in rural areas usually consists of passive or low-maintenance processes, such as trickling filters, rotating biological contactors and/or constructed wetlands (CW). However, these have limited ability to remove phosphorus (P) to the low levels (≤ 1 mg/L) that are required from the newly implemented water framework directive (WFD) (EU Water Framework Directive 2000) across Europe. Therefore, alternative options that can remove P whilst maintaining the low maintenance and chemical inputs in an economically viable way are highly desired. Adaptation of CW using reactive media to replace gravel has been investigated in this regard due to the media's ability to remove P from wastewater through precipitation and adsorption mechanisms (Vohla *et al.* 2011). A comparison of the media previously tested indicates that those rich in Ca/CaO, such as steel slags, show higher P retention capacities than the alternative media (Gubernat *et al.* 2020). Particular attention has been given to blast oxygen furnace (BOF) steel slags which are a waste material from steel making and hence offer a solution aligned to circular economic thinking.

Previous research into the use of steel slag has involved systems covering a range of scales from laboratory to pilot trials (0.98–6,000 L), operating across a wide range of contact times (empty bed contact time, EBCT = 3–226 h) and treating predominately synthetic wastewater with only a few studies using real wastewater (Table S1 in Supplementary Information). The wide ranges of media size used (0.1–50 mm) and initial P concentration

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(2.3–300 mg/L) reported in the literature are making the comparison between these different studies difficult (Johansson Westholm 2006; Vohla *et al.* 2011). For instance, reported P retention capacities for non-saturated media ranged from 0.085 mg P/g media (Hussain *et al.* 2015) up to >10.52 mg P/g media (Dunets *et al.* 2015) while the highest reported value for saturated media was 3.1 mg P/g media (Blanco *et al.* 2016). A study comparing samples from 10 European production sites revealed basic oxygen furnace slag (BOF) to deliver a higher P retention of 2.49 mg P/g media compared to 0.28 mg P/g media for electric arc furnace slag (EAF) (Barca *et al.* 2012). Further, the study showed that the samples from the different sites lead to variation in performance as illustrated in the range of retention capacity for BOF between 1.14 and 2.49 mg P/g media. To date, there has been one reported trial with real wastewater in a pilot-constructed wetland with BOF, where the reported performance (0.61 mgP/g media) was significantly lower than that reported for synthetic wastewater trials (up to 2.49 mg P/g media) (Barca *et al.* 2012, 2013). The only other large-scale, long-term study utilised melter slag which removed 70% of the incoming P for 5 years when operating at a 7-day EBCT. Thereafter, performance deteriorated reaching a final retention capacity of 1.23 mg P/g media (Shilton *et al.* 2006). Overall, this highlights the need for testing in real conditions in terms of scale and wastewater to ensure a realistic and robust assessment of the technology. Furthermore, a number of previous studies have proposed potential mechanisms by which the phosphorus is removed (Figure 1). They all indicate the predominant mechanism to be calcium oxide dissolution followed by calcium phosphate precipitation resulting in the formation of hydroxyapatite (HAP) (Barca *et al.* 2012; Claveau-Mallet *et al.* 2018). In addition, adsorption onto the formed HAP and ligand exchange with metal hydroxides have been identified but are assumed to be relatively minor. However, the experiments leading to the proposed mechanisms were conducted in synthetic waters with elevated phosphorus concentrations, potentially generating misrepresentative findings (Molle *et al.* 2003). Again, a detailed evaluation of a system tested in real conditions of scale and wastewater characteristics will further elucidate the mechanisms involved.

Accordingly, there is a need to examine the performance of BOF slag, found to perform the best of all media tested, under realistic scales and conditions to establish the potential for the technology to be used at full scale and to validate the proposed mechanisms. The current paper aims to achieve this through the examination of a full-scale CW containing BOF steel slag (from a source not previously reported on) operated with a real municipal wastewater effluent providing more realistic treatment conditions of wastewater characteristics and P concentrations. The study lasted for 782 days and included analyses of the effluent quality, mineralogical properties of the media and reed development. To the authors' knowledge, this is the largest and longest reported study using BOF steel slag for P removal in CW.

MATERIALS AND METHODS

Constructed wetland

A full-scale horizontal sub-surface flow wetland (Figure S1 in Supplementary Information) filled with BOF steel slag media (99,600 kg, $d = 8\text{--}14$ mm, Lafarge Tarmac Trading Ltd, UK) (no pre-treatment of the media was

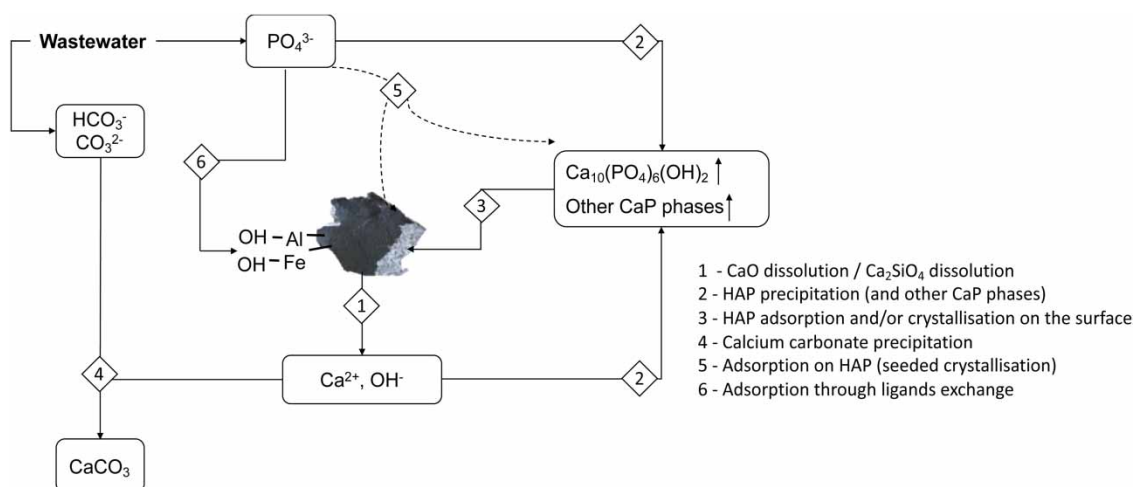


Figure 1 | Proposed mechanisms based on literature. Adapted from Barca *et al.* (2012).

carried out) was operated as a trial plant for 782 days at a sewage treatment works in Leicestershire, UK. The wetland was built according to a typical tertiary design in the UK with a surface area of 100 m² (width: 8 m, length: 12.5 m) and 0.6 m depth. The bed was planted with *Phragmites australis* at 4 plants/m² which were not harvested throughout the trial. The influent of the system was the effluent of secondary clarifiers and P was supplemented to an influent P concentration of 5.8–9.5 mg P/L (Table 1). This would simulate the P concentration in a small sewage treatment works with no or limited P removal where a wetland would normally be installed. The bed was operated at a flow rate of 0.35–0.7 L/s equating to an EBCT of 24–48 h. The effluent from the system was blended with the effluent from other phosphorus removal trial plants and the effluent from the sewage treatment works prior to discharge to the receiving water to ensure that the regulatory requirements were met at all times at the site.

Wastewater analysis

Online monitoring was set at the wetland influent and effluent for ortho-P, Fe³⁺, pH, turbidity, flow rate and temperature (influent only). Additional weekly grab samples were taken for analysis of P and chemical oxygen demand (COD) fractions (solid, colloidal, dissolved), total P (TP), total suspended solids (TSS), alkalinity pH, and metals. The metals analysed were Ca, Fe, V, Ni, Cu, Zn, As, Ag and Cd. The online analysis of P and Fe³⁺ was conducted according to colorimetric techniques at 15 min intervals (ABB online analysers, UK). Turbidity and pH were analysed with online sampling probes at 1-min intervals (Hach, UK). The additional samples were analysed through the standard methods with cell tests according to colorimetric methods for P, COD, Fe³⁺ and NH₄⁺ (Hach, UK). It should be noted that the samples were acidified for the Fe³⁺ and metals analysis to ensure measurement of the soluble forms. Repetition of some of the analyses with the online monitoring and grab samples allowed us to validate the results obtained. Fractions for P and COD were divided into unfiltered and filtered through 1.2 µm and 10 kDa representing solid, colloidal and dissolved fractions, respectively. Suspended solids were measured according to standard methods. pH was measured with a handheld probe meter (VWR, UK). Metals were analysed with an ICP-MS (Perkin-Elmer, UK). All analytical tools were calibrated regularly and wherever applicable (e.g. ICP for the metals) certified standards were used and all samples were analysed in triplicate to ensure accuracy of the measures.

Hydraulic assessment

To assess the change of retention time and possible clogging within the bed, tracer and hydraulic conductivity tests (HCT) were undertaken. Tracer tests were conducted by injecting a pulse of a known weight of Rhodamine-WT (Keystone, UK) and measuring the concentration of the chemical in the effluent with a rhodamine detector probe (YSI, Xylem, UK) over a duration of 2 days. The HCT was performed as described by Pedescoll *et al.* (2009) by inserting a steel tube into the bed, filling it with 5 L of water and measuring the decrease of the water level with a levellogger (Model 3001, Solinst, Canada). Hydraulic conductivity was measured at 12 points throughout the bed (Figure 2) to ensure a reliable assessment of the conditions throughout the bed.

Media and visual plant analysis

Photographs of the wetland were taken weekly to monitor visual changes in plant growth over time and with the seasons. Rainfall and ambient temperature were monitored on site with a weather station.

Table 1 | Wetland influent characteristics

	Number of samples (n)	Average ± standard deviation
COD (mg/L)	78	21.3 ± 2.8
Total P (mg/L)	80	7.68 ± 0.95
Ortho-P (mg/L)	122	7.63 ± 1.83
Suspended solids (mg/L)	76	7.3 ± 3.4
Ca ²⁺ (mg/L)	73	60.66 ± 12.33
Alkalinity (mg/L)	15	178.08 ± 16.34
pH	79	7.13–7.91
Fe ³⁺ (mg/L)	55	0.05 ± 0.07

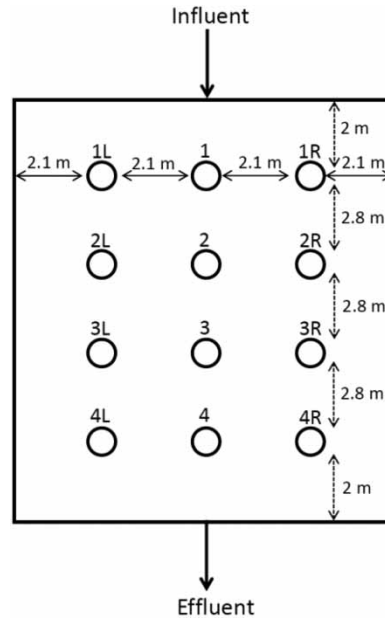


Figure 2 | Layout of sampling points for hydraulic conductivity test and samples for SEM/energy dispersive X-ray spectrometry (EDX) and sequential P extraction.

Sequential P extraction experiments were carried out with steel slag samples following the method described by Letshwenyo (2014) using 1 M NH₄Cl, 0.1 M NaOH, 0.5 M NaHCO₃, 1 M HCl and concentrated HCl to desorb loosely bound P, Al bound P, Fe bound P, Ca bound P and P in stable residual pools, respectively. Samples of fresh, unused slag and exhausted slag at the end of the trial were analysed. Fresh steel slag samples were divided into unused (FU) and washed (FW), i.e. washed three times with 25 mL de-ionised (DI) water and air dried for 3 days. The exhausted slag samples were taken from four points in the direction of flow (Figure 2). All slag samples (1 g each) were air dried for 24 h before the commencement of the procedure, shaken for 24 h in each extraction solution and washed with 25 mL of supersaturated NaCl in-between steps. Analysis was conducted with respect to 0.45 µm filtered TP measurements. Solutions were also analysed for their metal content and the sum from each extraction solution was taken as the value of total extracted metal.

Precipitation diagnostics

The potential precipitates that could form during the trial were determined through the calculation of the saturation indices (SI) using MINTEQA version 3.1 as the ratio of the ion activity product (IAP) of a given mineral by its solubility product (Gustafsson 2016):

$$SI = \frac{[IAP]}{[K_{sp}]}$$

SI values were calculated in relation to the differences observed between inlet and outlet levels of calcium, ortho-P, magnesium, vanadium, aluminium, iron, silica, titanium, alkalinity and NH₄-N in combination with water temperature and pH on trial days 33, 121, 210, 253, 266, 329, 342, 352, 366, 406, 504, 581, 608, 685 and 749. Values of SI greater than 1 signified the potential to precipitate.

To complement this, the morphological and elemental composition of samples of unused and used steel slag was investigated using a scanning electron microscope coupled with an energy-dispersive spectrometer (ESEM, FEI XL30, Philips UK) operated with Aztec software (Oxford instruments NTS, Abingdon, UK). The scanning electron microscope (SEM) was operated at a voltage of 20 kv, spot 5 for imaging and analysis. The energy dispersive X-ray spectrometry (EDS), coupled to the SEM, was used to identify the elemental composition of the samples and provide information on their quantitative composition. The elemental composition was determined over the whole surface point of the sample. The EDS capture time was 60 s. Identification of the mineralogical composition of the media was conducted using an X-Ray diffractometer (Siemens, D5005 X-Ray diffractometer, UK). The XRD was operated at 10°–90° with slits of 2, 2 and 1 mm for an hour.

RESULTS AND DISCUSSION

Treatment performance

The concentrations of organics (21.3 ± 2.8 mg/L as COD), ammonia (<2 mgN/L) and TSS (7.3 ± 3.4 mg/L) were all very low in the influent (Table 1) and were all slightly reduced during treatment in the CW to 14.0 ± 1.9 mg/L for the COD and 2.5 ± 2.2 mg/L for TSS. The effluent from the reactive media CW was below 0.5 mg P/L for the first 6 months and further remained below typical target consents for small works of 1 and 2 mg P/L for 266 and 353 days. During the 782 days of the trial, four distinct phases were identified based on major changes in the effluent P, which lasted for about 6 months each (Figure 3).

In *phase 1* (days 1–209, P load from 0 to 0.47 mg P/g slag), the system achieved almost complete P removal with an effluent P concentration around 0.05 mg P/L (the detection limit). This coincided with a stable elevated pH of between 11 and 12 and a net calcium release of up to 37 mg/L (Figure 3(a) and 3(b)). Such conditions are

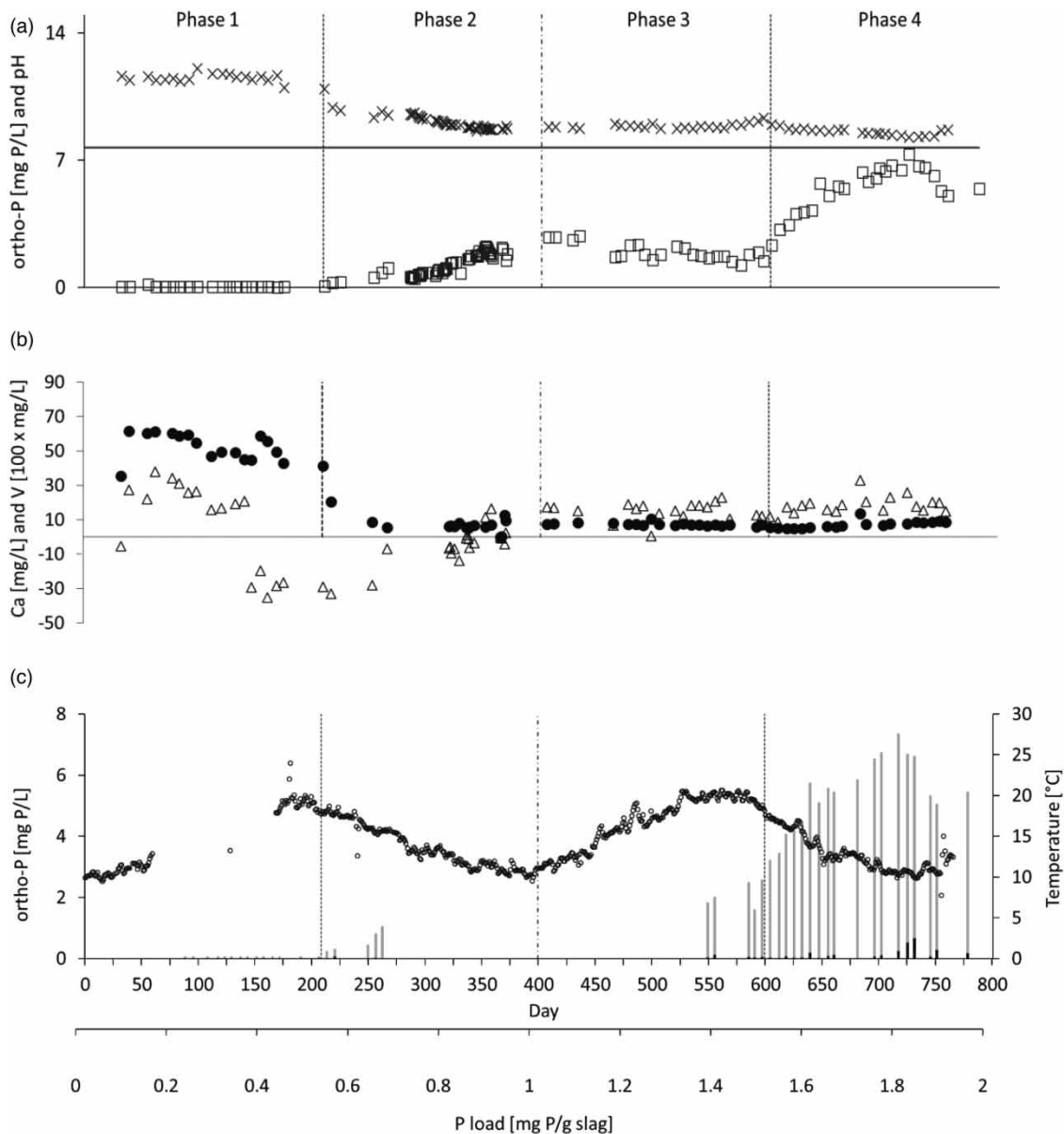


Figure 3 | Overview of main measured parameters during the whole period of operation. Changes in flow rate (and EBCT) were from 48 to 24 h EBCT on day 209 and from 24 to 48 h on day 278. (a) Average influent P (—, 7.63 ± 1.83 mg/L), effluent P (□) as ortho-P in mg P/L and effluent pH (X). (b) Release of calcium (Δ) and vanadium (●) reported as the difference between the influent and effluent concentrations (a positive value shows a release and a negative value shows an uptake). (c) Effluent P fractions: Particulate P (■) and dissolved P (▨) and water temperature (○).

consistent with the rapid dissolution of calcium oxide, leading to the formation of hydroxide ions and hence the increase in pH and subsequently precipitation of the released calcium (Johansson & Gustafsson 2000; Song *et al.* 2002). Towards the end of this phase of operation, the net calcium levels became negative indicative of continued precipitation and growth exceeding the rate of calcium release from the media and so utilising calcium from the incoming wastewater. In addition, other compounds were observed to be released from the media (Figure 3(b)). Most important is the metal vanadium which resulted in effluent concentrations of between 0.35 and 0.7 mg/L compared to an influent level that remained below 1 µg/L throughout. Vanadium levels in treated wastewater are not routinely consented as it is not expected to be present. However, potential limiting values around 60 µg/L have been discussed during other reported trials (Fonseca 2017). Accordingly, vanadium leaching poses a non-compliance concern if being considered for operational use. During this phase, substantial inhibition of reed development was observed due to competition with a weed identified as *Epilobium hirsutum* (Figure S2 in Supplementary Information). The plant is known to grow preferably in alkaline conditions whereas the reeds seemed dormant until the pH reached an acceptable level below 9 (Figure 3(a)) (Al-Farraj *et al.* 1984; Pérez-Fernández *et al.* 2006; Yin *et al.* 2016). At the back end of the bed, no reed growth was observed. It should be noted that according to the literature (Maucieri *et al.* 2020; Carrillo *et al.* 2022), plants have only a very limited contribution to phosphorus removal in CW and hence, it is assumed here that the removal observed throughout the trial was due to other mechanisms related to the presence of the reactive media.

In *phase 2* (days 209–400, P load between 0.47 and 1.01 mg P/g slag), the EBCT was decreased from 48 to 24 h. As the system performed extremely well in the first phase, the change of EBCT was implemented to evaluate if the system could still deliver such performance at a shorter contact time; however, this resulted in a gradual increase in the effluent P up to 1.96 mg P/L. On day 278 (equivalent to 0.73 mg P/g slag), the EBCT was reverted to 48 h to, in principle, reverse also the reduction in performance, but interestingly, the effluent P concentration continued to increase until a maximum of about 2.24 mg P/L after a P load of 1.01 mg P/g slag (400 days of operation). In parallel, pH in the effluent decreased to values of 8.6–8.7. The initial increase in effluent P concentration when the contact time was decreased is consistent with previous trials (Barca *et al.* 2013) although the continued increase when the contact time was reverted back was not expected based on the previous literature. The deterioration in removal performance coincided with an increase in the net calcium levels up to a maximum of 16 mg/L and a decrease in the corresponding levels of vanadium to below 100 µg/L on average across this phase of the trial. In addition, the effluent P increase, especially after a P load of 0.73 mg P/g slag, coincided with a drop-in temperature from 15.0 to 9.5 °C suggesting temperature as another impacting parameter on P removal (Figure 3(b) and 4(b)). In comparison, Blanco *et al.* (2016) reported a pH drop from 12 to 7 until a P load of 4.3 mg P/g slag was reached. The link between pH and removal has been verified in laboratory trials where steel slag particles have been soaked in sodium hydroxide and showed a significant reduction in P uptake below a pH of 8 (Park *et al.* 2017a). Overall, this phase is indicative of the precipitate coating the media restricting the rate of dissolution. Importantly, the pH and removal remained, albeit at a reduced level to phase 1, indicating that dissolution had slowed and not stopped. During this phase, the weed *Epilobium hirsutum* had overgrown the reeds up to the middle of the bed. At the back of the bed, both reeds and the weed sustained with little growth (Figure S2 in Supplementary Information).

In *phase 3* (days 401–600, P load between 1.01 and 1.44 mg P/g slag), the performance was relatively stable with the pH remaining between 8.7 and 9.3 and the effluent P slowly decreasing from 2.76 to 1.24 mg P/L. This change coincided with an increase in the water temperature from 11 to 20 °C (Figure 3(c)). Net releases of calcium and vanadium were consistently below 23 and 0.1 mg/L, respectively, suggesting a slow but steady release from the media (Figure 3(b)). This indicates a stable period where reasonable P removal can occur, which is thought to be mainly associated with growth or adsorption onto the precipitate that had previously formed. During this phase, plant growth of reeds increased at the back of the bed and weed growth at the front and middle ceased (Figure S2 in Supplementary Information).

In *phase 4* (days 601–782, P load between 1.44 and 1.86 mg P/g slag), the pH was stable with values between 8.9 and 8.7 and both the calcium and vanadium concentrations remained unchanged compared to phase 3. In contrast, a significant difference was observed for the effluent P concentration which increased up to a maximum of 7.33 mg P/L after 721 days of operation which meant nearly no P removal. From that point on, the effluent P concentration decreased rapidly again to reach a value of about 5.04–5.43 mg P/L at the end of the trial (782 days of operation, P load of 1.86 mg P/g slag) (Figure 3(a)). It should be noted that the influent P concentration

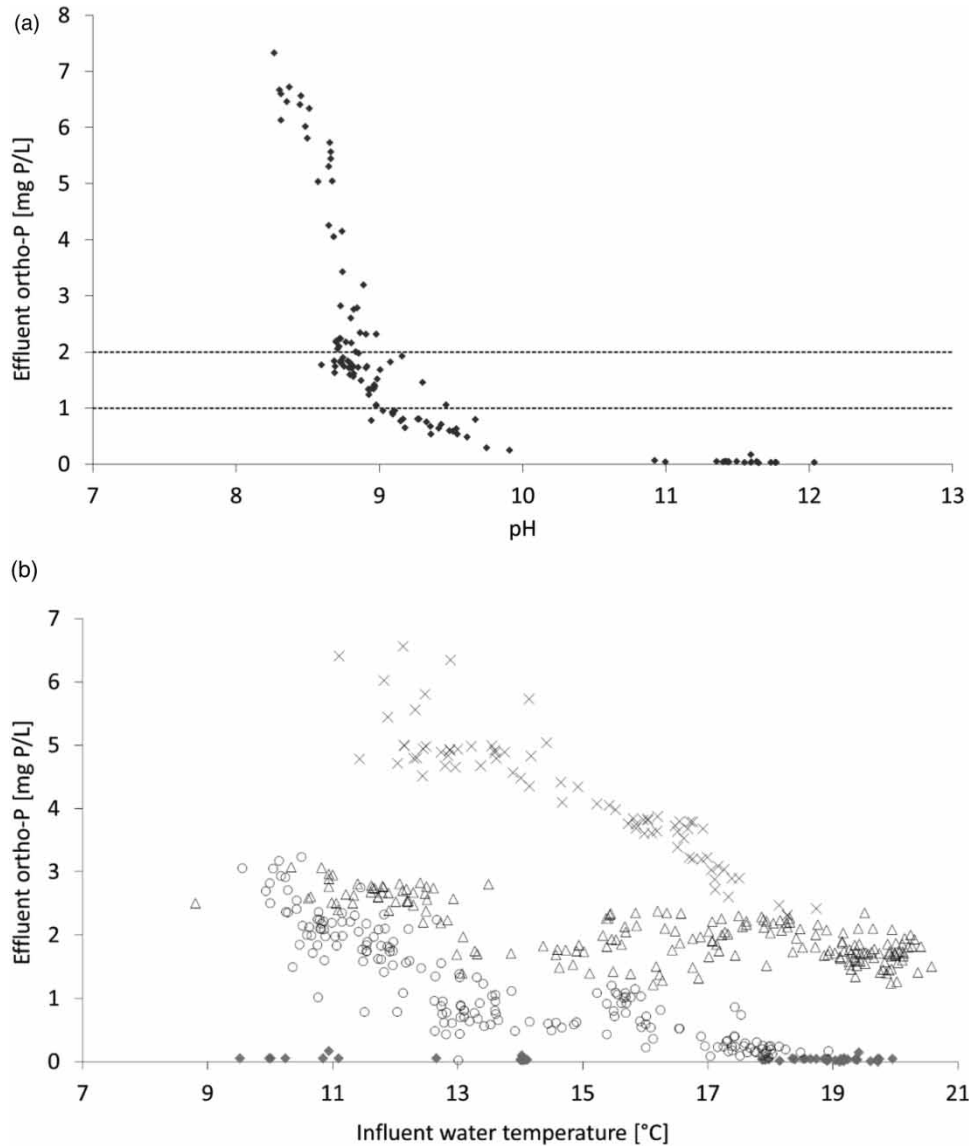


Figure 4 | Correlation of (a) effluent P with pH and (b) effluent P with temperature in phase 1 (◆), phase 2 (○), phase 3 (△) and phase 4 (X).

was found to fluctuate significantly over this last period with spikes of up to 12 mg P/L. Fractionation of the effluent P revealed that the majority existed as dissolved phosphate denoting that it is unreacted or had desorbed (Figure 3(c)). As in phase 3, the changes appeared to coincide with temperature changes, which is congruent with previous reports of seasonal impacts (Figure 4(b)) (Shilton *et al.* 2006; Barca *et al.* 2013; Herrmann *et al.* 2014). The respective authors have associated the changes to either temperature-dependent P removal mechanisms, due to the increasing growth of algae raising the pH (Shilton *et al.* 2006) or the change in the solubility of calcium phosphate with temperature (Barca *et al.* 2013; Herrmann *et al.* 2014). This is supported by the fact that the reaction of calcium and phosphate is endothermic which means that the chemical equilibrium would be shifted towards the product side (calcium phosphate precipitates) at higher temperatures and result in higher P removal (Stumm & Morgan 1996). During this phase of operation, most plant growth ceased at the front of the bed and the reeds were established from the middle to the back of the bed (Figure S2 in Supplementary Information).

The reactive media bed was observed to also impact on other metals in the wastewater with iron, zinc, nickel, copper, arsenic, silver, cadmium and lead levels reduced by up to 84, 35, 18, 22, 41, 71, 52 and 15%, respectively. This occurred despite their low initial concentration (on average <0.2 mg Fe/L and <0.027 mg/L of all other

metals) and indicates that other precipitates may have been formed other than calcium phosphate. However, the profile fluctuated through the trial relative to the different phases with uptake in phase 1 and release in phase 2 (Figure S3 in Supplementary Information). To illustrate, an uptake of zinc up to 56.9 µg/L was recorded in phases 1 and 3 while a release up to 35.7 µg/L was observed in phase 2. Uptake of other metals in phase one include 21.7 µg/L for copper, 1.8 µg/L for cadmium and 0.8 µg/L for lead. Comparatively lower release levels were observed in phase 2 at concentrations of 3.8, 0.32 and 0.51 µg/L, respectively. For arsenic, most variations were observed in phase 4 with fluctuations between 40.7 µg/L uptake and 40.9 µg/L release.

Further analysis of the link between pH and effluent phosphorus concentration revealed a decreasing trend (Figure 4(a)). Between pH 10 and 12, effluent P was stable below 0.25 mg/L and with decreasing pH from 10 to 8.3, the effluent P increased exponentially. Overall, it suggests that an effluent phosphate concentration below 2 mg/L only occurred when the pH was above 9. Below this level, the effluent P concentration changed significantly. In contrast, Park *et al.* (2017b) reported an ideal pH of >8 for P removal above 80% using steel slag which is consistent with the reported optimum pH range of 8.0–9.5 for calcium phosphate precipitation when the P concentration is below 5 mg P/L (Kim *et al.* 2006). The difference in the current dataset suggests a change in the removal pathway and a possible P removal mechanism related to the adsorption of phosphate to other precipitates (Giannimaras & Koutsoukos 1987). Further, if all removed P is assumed to have reacted to Ca₅(PO₄)₃OH, a stable pH between 10.1 and 11.1 can be predicted for the whole operational time. This only coincides with the actual measured pH in phase 1 suggesting that this might be the main P removal mechanism in that phase but not the subsequent ones.

Importantly, much of the previous work has been conducted in synthetic solutions and in the absence of carbonates. In the current case, the wastewater had an alkalinity of 178.1 ± 16.3 mg/L suggesting a relatively higher abundance of carbonates over phosphate. Accordingly, it is suggested that significant proportions of the precipitate were likely to be calcium carbonates. This was confirmed through SEM/EDX analysis of precipitates formed from a wash-out during commissioning, when no P was supplemented to the influent (data not shown) and more importantly during the analysis of the media taken from the bed (see next section on SI and materials analysis). In fact, Song *et al.* (2008) demonstrated an adverse impact of carbonate ions on calcium phosphate precipitation at pH 8 which, however, became negligible at more alkaline conditions (pH ≥ 9) showing that the pH is a key contributor. It is likely that lower P removal was not only caused by the pH decrease but also by less Ca²⁺ availability. The latter may have favoured CaCO₃ over calcium phosphate precipitation. For instance, Liira & Kõiv (2009) suggested that a doubling of retention time in shale ash columns resulted in supersaturation with respect to calcium carbonate. Despite being different media, steel slag and shale ash are both calcium-rich materials and it can be expected that the comparably high EBCT of this wetland (48 h during most of the study) did have an impact on calcium carbonate precipitation. Finally, these results highlight the need to monitor and understand the impact of carbonates on P removal and reactive media performance.

Further analysis of the media by sequential extraction supported the notion that reactions other than calcium phosphate precipitation were occurring. Compared to fresh slag, increases predominantly associated with the stable residual pool, iron bound, and loosely bound fractions were observed with an overall decrease associated with calcium bound P (Figure 5). To illustrate, the iron bound fraction increased from 2% in the fresh media to between 8 and 40% in the used samples. Equivalent changes in the stable residual pool saw an increase from between 0.2 and 0.7% to between 14 and 21%. This suggests that more consideration should be given to the P removal through other mechanisms such as incorporation into other minerals (e.g. iron-based ones), or adsorption.

By the end of the trial, the media had a P retention capacity of 1.39 mg P/g media (Figure 6). Of the available literature, only four studies provided higher overall P capacity, but all were at a significantly smaller scale (<3.4 L), with synthetic wastewater as feed and high influent P concentrations (>15 mg/L). Compared to the more realistic trials, the P retention capacity of this study was the highest reported to date (Table 1). At a P load of 1.07 mg P/g media, Barca *et al.* (2014) reported a slightly higher P retention capacity which may be due to the longer retention time in their system and the use of synthetic wastewater feed. Interestingly, when comparing a trial with real wastewater at a similar P load (1 mg P/g media), the current study had an about 1.3 times higher retention capacity (Barca *et al.* 2013). The differences reflect the potential impacts of the media source, scale and media/wastewater characteristics. Ultimately, this means caution must be applied when translating data between studies, suggesting that pilot trials are critical in understanding the efficacy of reactive media to any specific site.

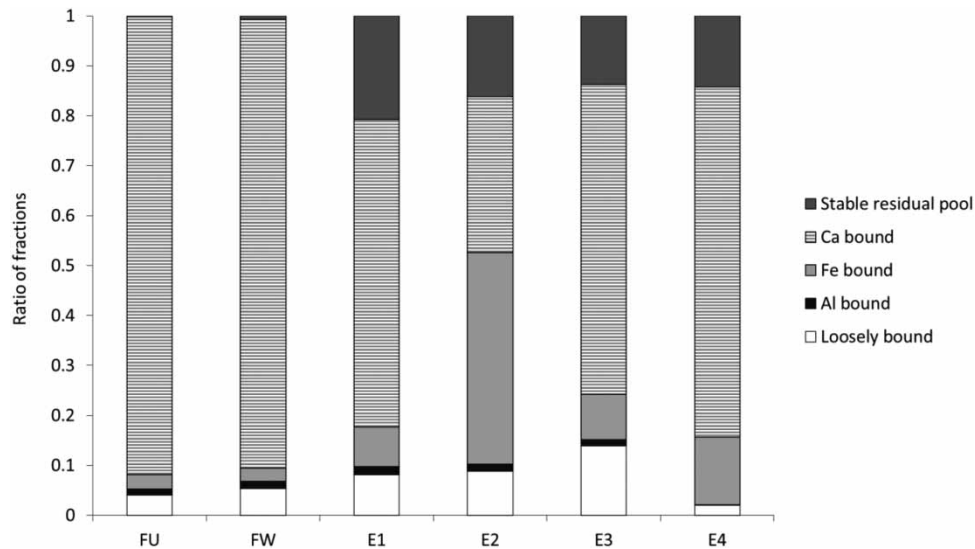


Figure 5 | Sequential extraction of P bound fractions from fresh unwashed (FU), fresh washed (FW) and exhausted (E) slag from four intersectional points (E1, E2, E3, E4).

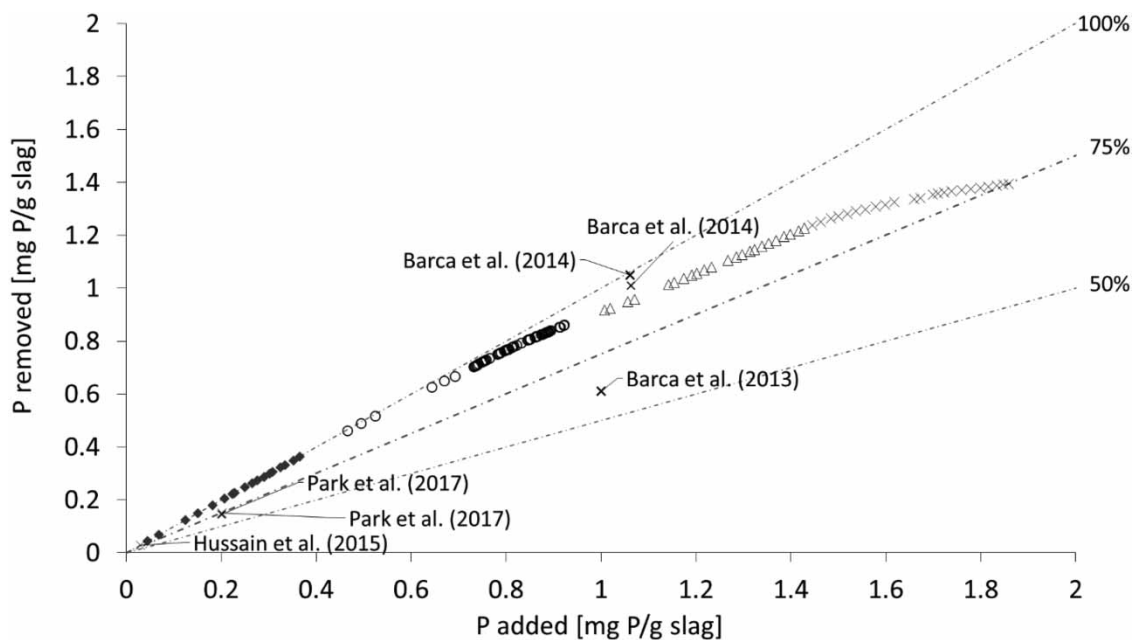


Figure 6 | Cumulative added and removed P in the reactive media reed bed in Phase 1 (◆), Phase 2 (○), Phase 3 (△) and Phase 4 (X) with comparison to literature (where data available).

SI and materials analysis

Across the entire trial potential supersaturation of 27–34 potential minerals was identified (Table S2 in Supplementary information). Many were associated with ferric oxides or calcium phosphates such as haematite (α -Fe₂O₃), HAP (Ca₅(PO₄)₃OH), magnesioferrite (MgFe₂O₄), maghemite (γ -Fe₂O₃), goethite (α -FeO(OH)), lepidocrocite (g-FeO(OH)), ferrihydrite (Fe₂O₃·0.5 H₂O) and Ca₃PO₄ (beta) as well as calcite.

Surface analysis of the used and unused media samples during the trial revealed changes in the elemental composition at the surface of the media, with in places reductions in calcium from about 40 wt% on the unused samples to between 16 and 32 wt% on the used samples (Figure 7) associated with a clear change in the morphology at the surface of the media. Reductions were also observed in terms of iron from about 6% to below 2% and magnesium (although present in a lower amount to start with), suggesting they were leaching from the

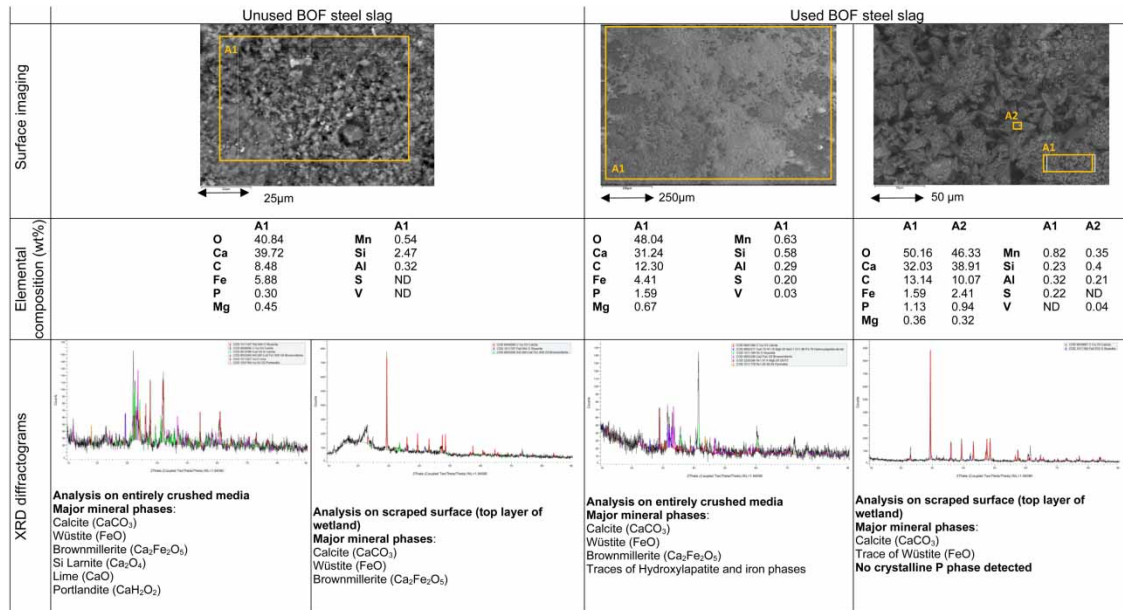


Figure 7 | Surface, elemental and mineralogical analyses of the unused and used BOF steel slag.

surface and forming precipitates with the reduction due to either the precipitates not forming on the media surface itself or the total amount being diluted by addition of other minerals. Further, when comparing the material from the surface and the internal structure of the unused media, the outer surface was rich in calcium and oxygen and showed lower levels of silica and iron. XRD analysis revealed this to be associated with calcite on the outer surface of the slag. This is congruent with natural weathering of the surface and uptake of carbon dioxide from the atmosphere (Navarro *et al.* 2010). Equivalent XRD analysis of surface only (scraped) and complete (crushed) material from the used media revealed only the presence of calcite on the surface and no indication of any P bearing minerals. In contrast, the crushed sample also contained other minerals such as wüstite, brownmillerite and portlandite. Overall, the analysis reveals the importance of carbonate reactions and in particular the formation of calcite which appears dominant on the surface with the potential impact on P removal occurring through a combination of adsorption or insertion into calcite crystals as well as the formation of amorphous phosphate minerals. Recent findings have shown that under the conditions that occur in these systems, phosphate will adsorb onto calcite followed by the formation of amorphous calcium phosphate (Li *et al.* 2017). Further, removal can continue in such cases as long as there is an available source of calcium in the wastewater to replenish sites for calcite-phosphate bonding (Bowden *et al.* 2009).

CONCLUSIONS

This study reports on the first long-term, full-scale BOF wetland operated with real wastewater in the UK. An ultimate retention capacity of 1.39 mg P/g media was observed with low effluent phosphorus concentrations achieved for around 1 year of operation. The high removal efficiencies were associated with elevated pH and concentrations of other trace metals inferring rapid dissolution from the media surface. The high pH then promoted the reactions for phosphorus removal through precipitation and adsorption on formed precipitate. As precipitates formed on the surface of the media, the dissolution of the calcium oxide into calcium and hydroxide ions in the water was reduced which led to a decline in the pH and calcium concentration in the water. Once this declined, removal also declined and became more responsive to temperature changes.

Ultimately, the experiences outlined in the current study identify some inconsistencies with previously reported studies and the associated mechanism of removal. Current predictions state that the main P removal mechanism is calcium phosphate precipitation with a potential phase transitioning from amorphous to crystalline at a later stage when P removal decreases. From the results in this study, it can be assumed that calcium phosphate is one of the P removal mechanisms, but it is suggested that calcium carbonate as well as magnesium and iron minerals can also precipitate, and these minerals may present adsorption sites for P. Accordingly, the work suggests key

consideration needs to be given to the impact of carbonates and the role of calcite on the removal of P from real wastewater.

In addition, the work has highlighted a number of challenges that need to be resolved before steel slag can be used as a P removal media in CWs. These include elevated pH, release of vanadium and the ability to sustain effective treatment for longer periods. It is posited that management of all three issues coincides with the ability to control the dissolution and release of calcium oxides from the media surface. Accordingly, the future focus needs to explore methods to deliver controlled precipitation onto the surface that mimics the natural weathering process but enables a controlled level of the initial release to maintain a long lasting controlled and steady removal of the phosphorus.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Al-Farraj, M. M., Giller, K. E. & Wheeler, B. D. 1984 Phytometric estimation of fertility of waterlogged rich-fen peats using *Epilobium hirsutum* L. *Plant Soil*. **81** (2), 283–289.
- Barca, C., Gérente, C., Meyer, D., Chazarenc, F. & Andrès, Y. 2012 Phosphate removal from synthetic and real wastewater using steel slags produced in Europe. *Water Res.* **46** (7), 2376–2384.
- Barca, C., Troesch, S., Meyer, D., Drissen, P., Andrès, Y. & Chazarenc, F. 2013 Steel slag filters to upgrade phosphorus removal in constructed wetlands: Two years of field experiments. *Environ. Sci. Technol.* **47** (1), 549–556.
- Barca, C., Meyer, D., Liira, M., Drissen, P., Comeau, Y., Andrès, Y. & Chazarenc, F. 2014 Steel slag filters to upgrade phosphorus removal in small wastewater treatment plants: Removal mechanisms and performance. *Ecol. Eng.* **68**, 214–222.
- Blanco, I., Molle, P., Sáenz de Miera, L. E. & Ansola, G. 2016 Basic oxygen furnace steel slag aggregates for phosphorus treatment: Evaluation of its potential use as a substrate in constructed wetlands. *Water Res.* **89**, 355–365.
- Bowden, L. I., Jarvis, A. P., Younger, P. L. & Johnson, K. L. 2009 Phosphorus removal from waste waters using basic oxygen steel slag. *Environ. Sci. Technol.* **43** (7), 2476–2481.
- Carrillo, V., Gómez, G. & Vidal, G. 2022 Phosphorus uptake by macrophyte plants in monocultures and polycultures in constructed wetlands for wastewater treatment. *Ecol. Eng.* **182**, 106690.
- Claveau-Mallet, D., Boutet, É. & Comeau, Y. 2018 Steel slag filter design criteria for phosphorus removal from wastewater in decentralized applications. *Water Res.* **143**, 28–37.
- Dunets, C. S., Zheng, Y. & Dixon, M. 2015 Use of phosphorus-sorbing materials to remove phosphate from greenhouse wastewater. *Environ. Technol.* **36** (14), 1759–1770.
- EU Water Framework Directive 2000 2000/60/EC.
- Fonseca, N. 2017 Sustainable phosphorus removal with BOF steel slag and apatite: Mechanisms and challenges. In: *AquaEnviro – Big P Conference*, 4th–5th July, Manchester, UK.
- Giannimaras, E. K. & Koutsoukos, P. G. 1987 The crystallization of calcite in the presence of orthophosphate. *J. Colloid Interf. Sci.* **116** (2), 423–430.
- Gubernat, S., Maslon, A., Czarnota, J. & Koszelnik, P. 2020 Reactive materials in the removal of phosphorus compounds from wastewater- a review. *Materials* **13**, 3377.
- Gustafsson, J. P. 2016 *Visual MINTEQ ver. 3.1. Stockholm*.
- Herrmann, I., Nordqvist, K., Hedström, A. & Viklander, M. 2014 Effect of temperature on the performance of laboratory-scale phosphorus-removing filter beds in on-site wastewater treatment. *Chemosphere* **117** (1), 360–366.
- Hussain, S. I., Blowes, D. W., Ptacek, C. J., Jamieson-Hanes, J. H., Wootton, B., Balch, G. & Higgins, J. 2015 Mechanisms of phosphorus removal in a pilot-scale constructed wetland/BOF slag wastewater treatment system. *Environ. Eng. Sci.* **32** (4), 340–352.
- Johansson, L. & Gustafsson, J. P. 2000 Phosphate removal using blast furnace slags and opoka-mechanisms. *Water Res.* **34** (1), 259–265.

- Johansson Westholm, L. 2006 Substrates for phosphorus removal-potential benefits for on-site wastewater treatment? *Water Res.* **40** (1), 23–36.
- Kim, E. H., Yim, S. B., Jung, H. C. & Lee, E. J. 2006 Hydroxyapatite crystallization from a highly concentrated phosphate solution using powdered converter slag as a seed material. *J. Hazard. Mater.* **136** (3), 690–697.
- Letchweno, M. 2014 *Phosphorus Removal in Passive Treatment Technologies for Tertiary Wastewater Treatment*. PhD Thesis, Cranfield University, UK.
- Li, Z., Sun, X., Huang, L., Liu, D., Yu, L., Wu, H. & Wei, D. 2017 Phosphate adsorption and precipitation on calcite under calco-carbonic equilibrium condition. *Chemosphere* **183**, 419–428.
- Liira, M. & Kõiv, M. 2009 The phosphorus – binding capacity of hydrated Ca Ca-oil-shale ash: Does longer retention time improve the process? *Dynam. Contr.* **43**, 3809–3814.
- Maucieri, C., Salvato, M. & Borin, M. 2020 Vegetation contribution on phosphorus removal in constructed wetlands. *Ecol. Eng.* **152**, 105853.
- Molle, P., Liénard, A., Grasmick, A. & Iwema, A. 2003 Phosphorus retention in subsurface constructed wetlands: Investigations focused on calcareous materials and their chemical reactions. *Water Sci. Technol.* **48** (5), 75–83.
- Navarro, C., Díaz, M. & Villa-García, M. A. 2010 Physico-chemical characterization of steel slag. study of its behavior under simulated environmental conditions. *Environ. Sci. Technol.* **44** (14), 5383–5388.
- Park, T., Ampunan, V., Maeng, S. & Chung, E. 2017a Application of steel slag coated with sodium hydroxide to enhance precipitation-coagulation for phosphorus removal. *Chemosphere* **167**, 91–97.
- Park, J., Wang, J. J., Kim, S., Cho, J., Kang, S., Delaune, R. & Seo, D. 2017b Phosphate removal in constructed wetland with rapid cooled basic oxygen furnace slag. *Chem. Eng. J.* **327**, 713–724.
- Pedescoll, A., Uggetti, E., Llorens, E., Granés, F., García, D. & García, J. 2009 Practical method based on saturated hydraulic conductivity used to assess clogging in subsurface flow constructed wetlands. *Ecol. Eng.* **35** (8), 1216–1224.
- Pérez-Fernández, M. A., Calvo-Magro, E., Montanero-Fernández, J. & Oyola-Velasco, J. A. 2006 Seed germination in response to chemicals: Effect of nitrogen and pH in the media. *J. Environ. Biol.* **27** (1), 13–20.
- Shilton, A. N., Elmetri, I., Drizo, A., Pratt, S., Haverkamp, R. G. & Bilby, S. C. 2006 Phosphorus removal by an ‘active’ slag filter—a decade of full-scale experience. *Water Res.* **40** (1), 113–118.
- Song, Y., Hahn, H. & Hoffman, E. 2002 Effects of solution conditions on the precipitation of phosphate for recovery A thermodynamic evaluation. *Chemosphere* **48**, 1029–1034.
- Song, K.-G., Kim, Y. & Ahn, K.-H. 2008 Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor. *Desalination* **221** (1–3), 467–474.
- Stumm, W. & Morgan, J. J. 1996 *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd edn. Wiley-Interscience, New York.
- Vohla, C., Kõiv, M., Bavor, H. J., Chazarenc, F. & Mander, Ü. 2011 Filter materials for phosphorus removal from wastewater in treatment wetlands – a review. *Ecol. Eng.* **37** (1), 70–89.
- Yin, X., Zhang, J., Hu, Z., Xie, H., Guo, W., Wang, Q., Ngo, H. H., Liang, S., Lu, S. & Wu, W. 2016 Effect of photosynthetically elevated pH on performance of surface flow-constructed wetland planted with *Phragmites australis*. *Environ. Sci. Pollut. Res.* **23** (15), 15524–15531.

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