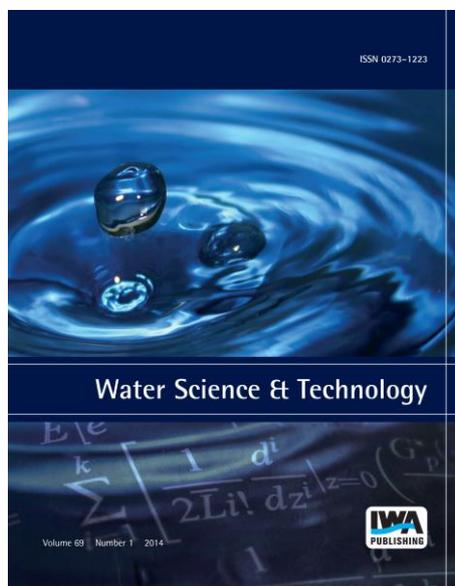


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Characterizing phosphorus removal from polluted urban river water by steel slags in a vertical flow constructed wetland

Yuan Ge, Xiaochang C. Wang, Mawuli Dzakpasu, Yucong Zheng, Yaqian Zhao and Jiaqing Xiong

ABSTRACT

Phosphorus (P) removal in constructed wetlands (CWs) is often low unless special substrates with high sorption capacities are used. However, the use of special substrates in vertical flow (VF) CWs has not been proved to enhance P sorption. Thus, two VF wetlands were designed to evaluate the potential for enhanced P removal from polluted urban river water, one with slag as substrate and the other as a control with gravel as substrate. Findings from batch experiments showed P sorption capacities of 3.15 gP/kg and 0.81 gP/kg, respectively, for steel slag and gravel. Different organic matter fractions played different roles in P sorption, the effects of which were significant only at high concentrations. Over a 220 days' operation, the VF-slag removed 76.0% of the influent total phosphorus (TP) at 0.159 g/m²-d and PO₄-P of 70.9% at 0.063 g/m²-d, whereas the VF-gravel removed 65.0% at 0.136 g/m²-d and 48.6% at 0.040 g/m²-d, respectively. Therefore, the merit of using a steel slag substrate in VF wetlands can be significant for the removal of PO₄-P.

Key words | phosphorus, slag, sorption, vertical flow wetland

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INTRODUCTION

Phosphorus (P) is ubiquitous in almost all wastewater types and represents a macronutrient of special importance for biological organisms in several ecosystems (Ding *et al.* 2015). However, high concentrations of P can have detrimental consequences in these ecosystems. Excessive concentrations of P are reported to be the most common cause of eutrophication in freshwater lakes, reservoirs, streams, and headwaters of estuarine systems (Correll 1998; Monteagudo *et al.* 2012; Ulrich *et al.* 2015; Pizarro *et al.* 2016). Eutrophication is a global problem, which often results in algal or cyanobacteria mats, anoxia (Correll 1998) and fish kills (Tekile *et al.* 2015), leading to greatly reduced biodiversity in water systems.

Constructed wetlands (CWs) have been used to treat several types of polluted water. Unsaturated vertical flow (VF) CWs are known to be efficient in the removal of total suspended solids (>90%), chemical oxygen demand (COD; >80%), biochemical oxygen demand (BOD₅; >90%). However, removal efficiencies of total P in VF CWs are typically less than 30% (Paing *et al.* 2015). Therefore, the search for

low-cost techniques to upgrade P removal in VF CWs has become a priority research focus.

The main P removal mechanisms in CWs are adsorption, precipitation, microbial conversion and plants' uptake (Richardson 1985; Moshiri 1993; Kadlec & Knight 1996; Korkusuz *et al.* 2007; Kadlec & Wallace 2009). Of these mechanisms, P adsorption onto substrates is widely known to be the most important removal pathway. The P sorption capacity of substrates is influenced by its physico-chemical characteristics such as mineral content (Fe, Al and Ca), particle size, specific surface area, and thus, the overall P removal rate (Drizo *et al.* 1999; Johansson *et al.* 1999; 2006). An effective substrate for P removal should possess not only a high mineral content but also a high electrical conductivity (Wang *et al.* 2013) and pH. Most substrates with pH >9 also have higher Ca content (>20%) (Vohla *et al.* 2011). Besides, the specific surface area, which increases with the decrease of particle size, can result in substrates with higher P adsorption sites (Lyngsie *et al.* 2014).

Gravel is a natural material, and the most common substrate used in CWs because it is cheap and readily available (Li *et al.* 2013). However, the relatively low mineral content of gravel means that removal efficiencies of total phosphorus (TP) and PO₄-P are typically low at only 4% and 1% in VF CW with gravel as substrate (Korkusuz *et al.* 2005). Hence, the search for suitable substrates is receiving research attention. Many industrial by-products, which have higher mineral contents than gravel, such as steel slag, fly ash and alum sludge, have been trialed in CWs in order to enhance the P removal efficiency (Zhao & Zhao 2009; Vohla *et al.* 2011; Ragheb 2013; Barca *et al.* 2014). Several recent studies (Drizo *et al.* 2006; Chazarenc *et al.* 2007; Lee *et al.* 2010; Barca *et al.* 2014; Name & Sheridan 2014) have demonstrated the potential of slag, a by-product of the steelmaking industry to enhance P removal. The high P removal capability of slag is attributed mostly to its CaO content, which is reported to range between 24.3–38.6% due to the different smelting methods (Sakadevan & Bavor 1998; Name & Sheridan 2014). The CaO reacts with P to form Ca-P precipitates.

In VF CWs, the use of substrates with special properties as stated above has not been proven to enhance the sorption of P (Stefanakis *et al.* 2014). This fact is influenced by the relatively short contact time between the wastewater and filter materials, which does not allow for intense adsorption and precipitation reactions to occur, and thus, require further research attention.

Typically, the P removal performance of substrates can be determined by measuring the maximal P sorption capacity, which can be obtained from batch sorption experiments (Sakadevan & Bavor 1998; Del Bubba *et al.* 2003). However, discrepancies in P removal performances for various substrates have been identified because of the differences in substrate physicochemical characteristics (e.g. content of mineral oxides, grain sizes and quantities) (Lyngsie *et al.* 2014). Therefore, P batch sorption experiments should be coupled with the assessment of substrate performance in column experiments to compare the P removal efficiencies and retention capacities by different substrates (Drizo *et al.* 2002; Wang *et al.* 2013).

While many recent studies have demonstrated the efficiency of steel slag as a substrate to enhance P removal from wastewater (Drizo *et al.* 2006; Chazarenc *et al.* 2007; Lee *et al.* 2010; Barca *et al.* 2014; Name & Sheridan 2014), only a few have been based on real wastewater (e.g. Barca *et al.* 2013). Most of these experiments were performed with synthetic P solutions, which did not contain all the components occurring in real wastewater or polluted river water that may affect P removal, such as organic matter (OM) and

competing anions. OM has been reported to potentially influence soil chemical and biological processes, and enhance P availability (Scheffe *et al.* 2009). More specifically, the organic acids such as oxalic, citric, tartaric and humic acids or other low molecular weight organic acids and organic colloids can block some surface-reactive sites on minerals, thereby reducing the P adsorption (Antelo *et al.* 2007). For calcareous substrates with a large reservoir of exchangeable calcium (Ca), precipitation of insoluble Ca-P phases, which predominate P removal, has been reported to be negatively influenced by the addition of OM (Braschi *et al.* 2003). This effect is particularly important for humic acid, an important dissolved OM that shows complex chemical compositions, reactivity and varying molecular weights (Lian *et al.* 2015). However, there is limited information on the fate of phosphate in the presence of such OM in CWs' substrates.

In this study, gravel and steel slag were used as substrates in two VF CWs to treat highly polluted urban river water. The river water contained complex OM constituents. The aim was to assess the P removal performance of VF CWs containing different substrates. The corresponding specific objectives were to: (1) evaluate the P sorption capacities of different substrates; (2) compare P removal performance of different substrates in column experiments; (3) identify the effects of organic acids and water-soluble OM on P sorption; and (4) assess factors affecting P removal in VF CWs with different substrates.

MATERIAL AND METHODS

Substrates

Preparation of substrates

Gravel was collected from the flood land near a river in Xi'an, China. Basic oxygen furnace (BOF) steel slag was purchased from a local steel plant (Shaanxi Iron and Steel (Group) Co. Ltd, Xi'an, Shaanxi, China). Each substrate was air-dried and manually-sieved into a geometrical mean particle size range of 0.5–1 mm. The sieved samples were washed with distilled water to remove the residual acid and soluble compounds. The cleaned slags and gravels were oven-dried at 15 °C for 24 h.

Characterization of substrates

The surface morphology and microstructure of the two substrates were examined by scanning electron microscopy

(SEM, JEOL, JSM-5800). X-ray fluorescence was used to determine the chemical composition mass percentage of each substrate. The pH of each substrate was measured using a pH meter after mixing 2 g of substrates with 10 mL deionized water. The specific surface area was measured using a nitrogen Brunauer–Emmett–Teller.

Batch sorption experiments

Potassium phosphate monobasic salt (KH_2PO_4) was dissolved in 0.02 M KCL to prepare stock solutions. 2 g of substrate material (particle, 0.5–1 mm) were added to a 150 mL Erlenmeyer flask containing 50 mL of sorbate solution. The Erlenmeyer flasks were shaken for 48 h at 25 °C and 150 rpm. The supernatants were filtrated with 0.45 μm membrane filters and ready for P measurement. All the sorption and control experiments were conducted in parallel. The effects of initial pH and counter OM were investigated by varying the initial pH (2–10) and counter OM (citric acid, glucose, oxalic acid, humic acid), respectively.

Isotherm studies

A series of 50 mL sorbate solutions with nine different initial concentrations of 2, 5, 10, 20, 50, 100, 150, 200, 400 mg/L were agitated with 2 g of substrates at 150 rpm for 48 h. The amount of P sorbed to the substrate was calculated according to Equation (1).

$$Q_e = (C_i - C_e)V/M \quad (1)$$

where Q_e is the amount of P sorbed to substrate (mg P/kg), C_i is the initial concentration of P (mg/L), C_e is the final concentration of P or equilibrium concentration (mg/L), V is the volume of stock solution, and M is the mass of substrates.

Kinetic studies

Here, 2 g of substrate and 50 mL of sorbate solution of 5 mg/L were added to the Erlenmeyer flasks. The Erlenmeyer flasks were shaken in a digital water bath oscillator at 150 rpm for different time intervals of 0.5, 1, 2, 4, 6, 8, 10, 12, 16, 24, and 48 h. The amount of P sorbed to the substrate at time t , Q_t (mg/g), was calculated using Equation (2):

$$Q_t = (C_i - C_t)V/M \quad (2)$$

where C_t is the concentration of P (mg/L) at time t .

Laboratory-scale VF CW

Two laboratory-scale down-flow VF CWs with dimensions of length, 55 cm; width, 55 cm; height, 65 cm (Figure 1) were installed in March 2013 at a university in Xi'an, China. The two systems were filled with either BOF steel slag or gravel substrates of the same size grading (5–30 mm) as follows: the drainage layer (height of 0–15 cm from the bottom) was filled with 15–30 mm substrates, the middle layer (height from 15 to 40 cm) was filled with 5–15 mm substrates, and the top layer (40–55 cm) was filled with 15–30 mm substrates. The two substrates were washed with tap water before use in the pilot experiment.

Using a peristaltic pump, water from a highly polluted urban river near Xi'an was pumped from a storage tank to the two VF systems at a hydraulic loading rate of 0.05 m/d. The two VF wetlands were planted with local *Phragmites australis* (common reed) at a density of 13 shoots/m². The two systems were operated with unsaturated flow by continuous feeding for a total of 220 days. During the experimental period, total P and $\text{PO}_4\text{-P}$ were measured weekly from the influent and effluent of the two systems. TP was analyzed according to the molybdenum-antimony anti-spectrophotometric method, following digestion with potassium persulfate. $\text{PO}_4\text{-P}$ was measured according to the molybdenum-antimony anti-spectrophotometric method (MEPC & WWMAA 2002).

During the experimental period, although most of the plants survived, their growth and development in the slag system were found to be significantly limited, possibly due to the highly alkaline conditions. Over the 220 days of operation, the pH in the slag system was stable at about pH 8.5 (Figure 6(c)). Therefore, detailed analyses of the contribution of plants were not considered in this study.

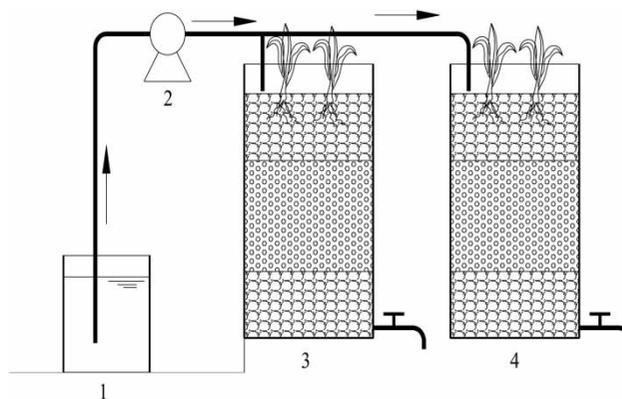


Figure 1 | Schematic diagram of VF CWs (1 = influent feed tank, 2 = peristaltic pump, 3 = VF-slag, 4 = VF-gravel).

Table 1 | Physical and chemical properties of slag and gravel

Substrate	Porosity %	True density (g/cm ³)	Bulk density (g/cm ³)	pH*	Surface area (m ² /g)	Chemical composition mass percentage %							
						CaO	SiO ₂	MgO	Na ₂ O	Al ₂ O ₃	K ₂ O	TiO ₂	Fe ₂ O ₃
Slag	49.4	3.1	1.4	10.6	4.3	37.8	21.8	5.5	–	16.9	–	1.1	13.1
Gravel	48.2	2.8	1.6	8.8	2.81	1.1	61.6	1.8	1.6	17.9	5.4	–	7.6

*pH was measured by mixing 2 g of substrates with 10 ml deionized water.

Nevertheless, many previous studies generally report that the amount of P removed by plants' uptake and subsequent harvesting of the produced aboveground plant biomass is negligible compared to the total removed amount (Stefanakis *et al.* 2014).

RESULTS AND DISCUSSION

Characteristics of substrates

As shown in Table 1, the two substrates had similar porosity, which were within the range of 40–66.4% reported in previous studies (Westholm 2006; Jha *et al.* 2008). Also, the bulk densities of the slag (1.4 g/cm³) and gravel (1.6 g/cm³) used in this research were within the range of 0.62–1.8 g/cm³ reported in previous studies (Wang *et al.* 2013; Barca *et al.* 2014). The surface area of slag was bigger than gravel (Table 1), and the SEM images (Figure 2) showed that the surface of slag was coarser than that of gravel. The coarser surface of slag indicated a stronger sorption capability, which would be beneficial to physical filtration and microbial growth.

Table 1 shows that the slag was mainly composed of calcium oxide (CaO), silicon oxide (SiO₂) and ferric oxide (Fe₂O₃), while the main composition of gravel was SiO₂ and Al₂O₃. Although the Al contents of both substrates were similar, the higher amount of Ca and Fe in slag implied a much higher potential for P removal from polluted water (Xue *et al.* 2009; Li *et al.* 2013). Previous studies have shown that most CWs substrates with high pH also had higher Ca content (>15%) (Vohla *et al.* 2011). P reacts differently with various metal ions under varying pH conditions. In alkaline substrates, Ca ions are released to form Ca-phosphates, which precipitates on the substrate surfaces. Therefore, the higher pH of slag than gravel indicated that slag would achieve better P sorption capacity.

Effect of OM

CWs received a significant amount of OM from the influent, and through the degradation of plants, decomposition reaction by microbes and secretions from plant roots, which may compete with P for substrate sorption sites (Huang *et al.* 2003). In the case of citric acid, the OH[–] can easily combine

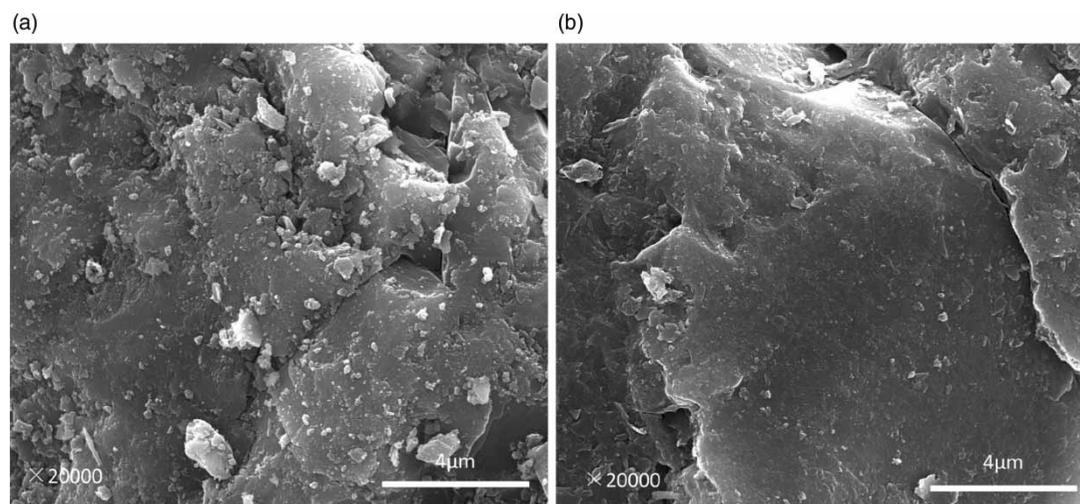


Figure 2 | SEM images of the substrates (a) slag, (b) gravel.

with Fe and Al, which could inhibit the chemical combination of P and Fe or Al. Previous research shows that humic substances could inhibit the P sorption at the beginning of the experiment. This inhibition then becomes weaker with time, which eventually changes to promote the P sorption (Gerke 1993). Therefore, different types of organic acids could express various effects on P sorption by substrates such as slag and gravel under different experimental conditions.

The main OM fractions in CWs were citric, oxalic and humic acids (Wang et al. 2012). In addition, glucose is a common OM in people's daily life. Therefore, the effects of these four types of OM on the P sorption of the two substrates were evaluated (Figure 3). For slag, the effects of glucose and oxalic acid were limited with Q_e of about 0.12 mg/g. Citric acid showed a strong inhibitory action when the initial concentration increased to above 5 mmol/L. Humic acid showed a similar effect as citric acid, albeit slightly weaker. The effects of glucose showed small fluctuations (Figure 2(b)). Unlike slag, oxalic acid promoted the P sorption of gravel to some extent. When the initial concentration was 20 mmol/L, Q_e was 1.5 times higher than that of the sorbate solution, which did not contain any OM. The mechanism of OM effects on P sorption by substrates could be explained by the competition for sorption sites (Huang et al. 2003). Although the main mechanism of P removal by slag is related to Ca-P precipitation, this process is also complemented by P adsorption by the high proportions of Al_2O_3 (16.9%), Fe_2O_3 (13.1%) and MgO (5.5%) present in the slag (Table 1). The presence of high contents of Al, Fe, Ca and Mg oxides in the slag media increases adsorption and precipitation reactions of P, which are

considered as coupled processes (Stefanakis et al. 2014). Humic acid includes many functional groups such as carboxyl, hydroxyl, carbonyl, benzoquinonyl, methoxy and so on. These functional groups can combine with the metal ions to occupy the sorption sites. For the chemical structure of citric acid, the more OH^- made it easier to combine with Fe and Al, which inhibited the chemical combination between P and Fe and Al. Previous research findings show that the P sorption could be inhibited by humic substances at the beginning of the experiment (Gerke 1993). However, the inhibition became weaker with time, which finally changed to promote P adsorption (Gerke 1993). Therefore, different types of organic acids could express various effects on P sorption by substrates such as slag and gravel under different experimental conditions.

Isotherm

The initial concentration was varied over the range of 2–400 mg/L to investigate the effect of different initial concentrations on P sorption. As shown in Figure 3(a), the Q_e of both substrates increased with the increase of initial P concentration. At initial concentration within the range of 2–50 mg/L, the percentage removal of P by slag was more than 90%. For gravel, the percentage removal decreased from 21 to 11%. When the concentration of P was increased from 50–400 mg/L, the removal efficiency of slag decreased drastically (Figure 4(a)).

The isotherm data were fitted to the Langmuir and Freundlich isotherm equations and the estimated model parameters with the correlation coefficient (R^2) are shown in

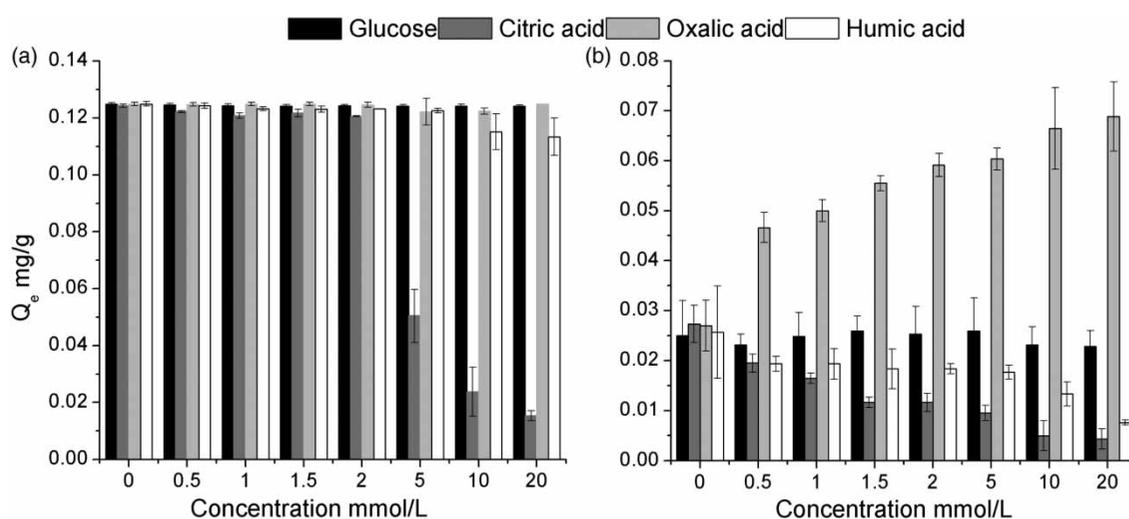


Figure 3 | Effect of OM on P sorption for the two substrates (a) slag, (b) gravel.

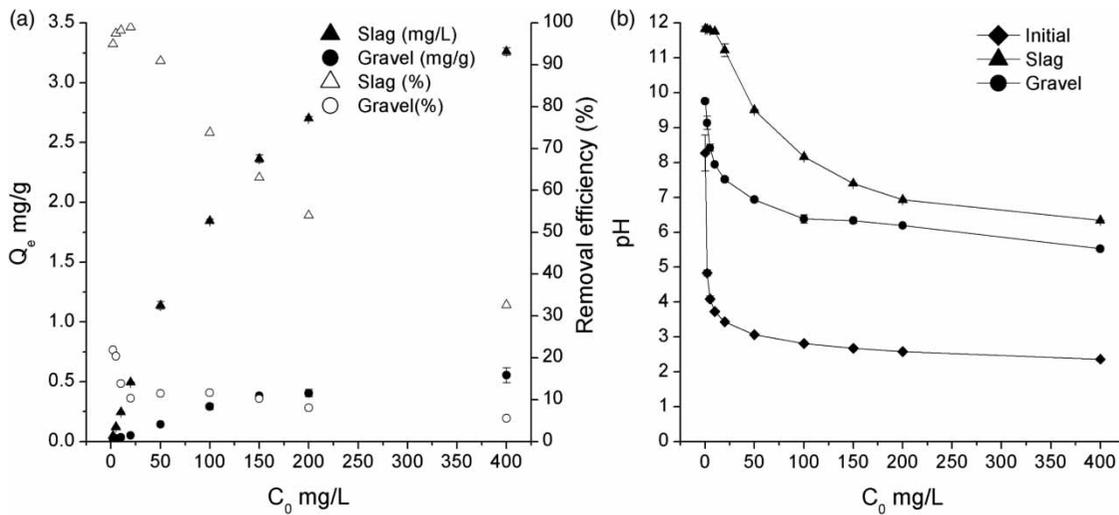


Figure 4 | Effect of (a) initial concentration on sorption of P by slag and gravel, (b) variation of pH during the sorption process.

Table 2. It is shown that the experimental data of P sorption on the two substrates were well fitted by the two isotherms. However, the Freundlich isotherm equation provided better fitting coefficients for slag, whereas the Langmuir equation was better fitted for gravel. This finding indicates that surface adsorption and diffusion into the particles functioned together for P sorption by slag. The Q_m of slag and gravel were 3.15 mg/g and 0.81 mg/g, respectively, which was consistent with previous findings (Xu et al. 2006; Xue et al. 2009). K_F is a relative indicator of the sorption capacity, representing the amount of P sorbed to the substrate. As shown by the Freundlich K_F value in Table 2, the sorption capacity of slag was higher than that of gravel. The $K_L \cdot Q_m$ of slag was also higher than that of gravel, which indicated that the P sorption of slag is much more stable than that

of gravel (Zhao 2007). Compared to previous studies, the slag used in this study achieved a higher P sorption (Sakadevan & Bavor 1998; Li et al. 2013). The P sorption capacity of substrates was related to the pH and Ca^{2+} , which has been widely reported in literature (Johansson 1999; Drizo et al. 2006). For different species of slags, such as blast furnace slag and steel furnace slag, the different smelting processes and products can considerably influence the P sorption capacity (Barca et al. 2014).

Kinetics of P sorption

Figure 5(a) shows the P sorption profile of the two substrates for a solution containing 5 mg P/L. The sorption capacity and rate of slag were significantly higher than that of

Table 2 | Langmuir and Freundlich isotherm constants and regression coefficients for the sorption of P

Substrates	Langmuir ^a				Freundlich ^b		
	K_L	$Q_m/(mg/g)$	$K_L \cdot Q_m$	R^2	K_F	n	R^2
Slag	0.074	3.15	0.233	0.956	0.674	3.406	0.974
Gravel	0.006	0.81	0.005	0.993	0.019	1.718	0.966

^aLangmuir isotherm equation:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

^bFreundlich isotherm equation:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where, K_F and n represent Freundlich sorption capacity constant and Freundlich intensity constant, respectively. K_L and Q_m are constants related to the affinity of the binding sites and the amount sorbed to substrates at equilibrium (mg/g), respectively. The Langmuir isotherm model assumes monolayer sorption onto a homogeneous surface containing a finite number of sorption sites. In contrast, the Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage (Chong et al. 2013).

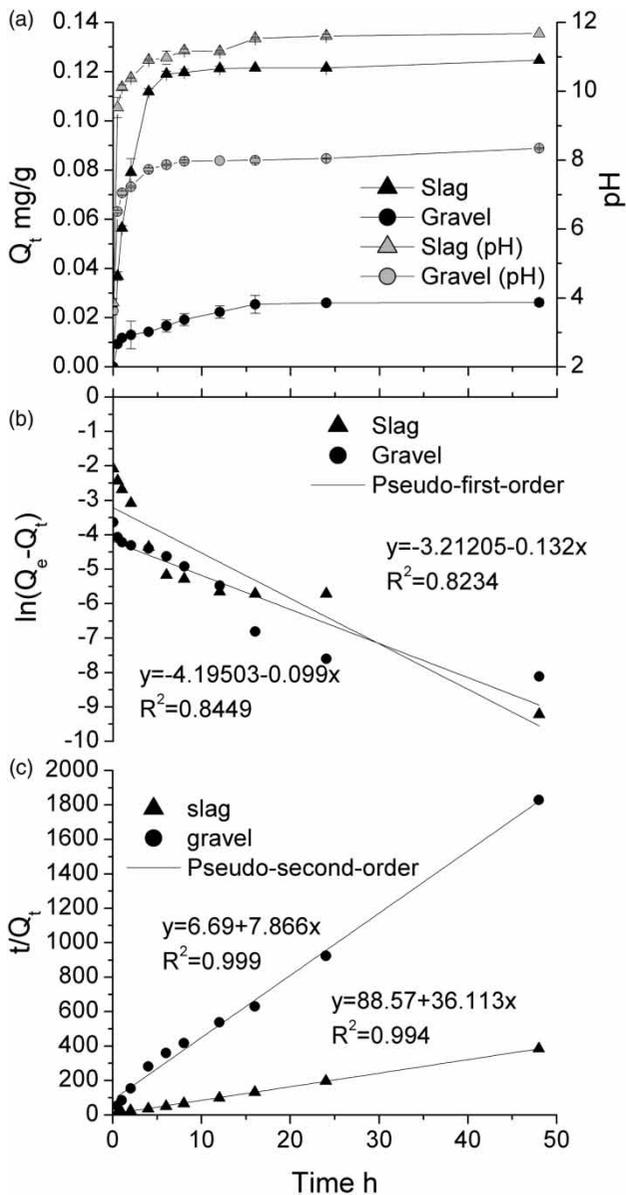


Figure 5 | (a) Effect of contact time on P sorption and the variation of solution pH, (b) pseudo-first-order and (c) pseudo-second-order kinetic models for P sorption of slag and gravel.

gravel. It was observed that the P sorption rate was rapid during the first 6 hours for the two substrates due to the presence of large amounts of empty binding sites. Over time, the sorption rate reduced until equilibrium was achieved at 24 h, whereby additional contact time did not result in any significant increase in sorption. The reduction in sorption rate is explained by the reduced amount of available empty binding sites. In addition, the variation of pH during the sorption process was similar with the increase of Q_t . During the sorption process, the rate of increase in pH was rapid in the first 6 h, which then became slower.

Findings indicate that the sorption capacity was closely related to solution pH. Thus, the Ca ions were released from substrates with shaking time, which effectively increased the sorption capacity of the substrates (Barca et al. 2014).

The experimental data of both substrates fitted well to the pseudo-second-order model (Figure 5(c)) with high correlation coefficients (R^2) of over 0.99. The result suggested that chemisorption could be a rate-limiting factor (Yao & Chen 2014). Furthermore, the sorption rate constants, k_1 and k_2 of 0.132 and 9.49 for slag, and 0.099 and 14.73 for gravel, respectively, indicated that slag achieved much higher and faster P sorption than gravel.

P removal in laboratory-scale vertical CW

For the operation period of 220 days, the TP, PO_4 -P and pH at the influent and effluent of the two VF CWs are shown in Figures 6(a), 5(b) and 5(c). At the beginning of the operation, the P removal efficiencies in the two CWs were similar. This finding was different from that of many previous studies, which reported that the slag unit achieved higher P removal at the beginning than gravel, and then decreased over time (Korkusuz et al. 2007; Li et al. 2013). According to our findings, more Ca ions were released from the substrates over time. Consequently, the P removal in VF-slag increased to exceed that in VF-gravel after 80 days. The average removal efficiencies of TP and PO_4 -P were 76% and 70.9% in VF-slag, and 65% and 48.6% in VF-gravel, respectively. The removal efficiencies were similar to those reported in previous studies (Chazarenc et al. 2007). The average total P removal rates were 0.159 $g/m^2 \cdot d$ and 0.136 $g/m^2 \cdot d$ in VF-slag and VF-gravel, respectively, whereas those for PO_4 -P were 0.063 $g/m^2 \cdot d$ and 0.040 $g/m^2 \cdot d$, respectively. The overall average total P removal was 0.048 g/d and 0.041 g/d, respectively. This result was slightly different from that of the experimental sorption data. The main reason was that although sorption by substrates could be the dominant mechanism in the CWs, which are complex eco-systems, the action of plants and microbes could affect the P removal to some extent.

The average pH of the influent was 7.53 ± 0.43 , which increased in the effluent of two VF CWs at 8.43 ± 0.55 and 8.0 ± 0.48 (Figure 6(c)). The higher pH of the effluent than the influent indicated that Al-P and Fe-P oxides were less available forms when compared to the Ca-P (Korkusuz et al. 2007). This potentially explains why the VF-slag performed better for P removal than VF-gravel.

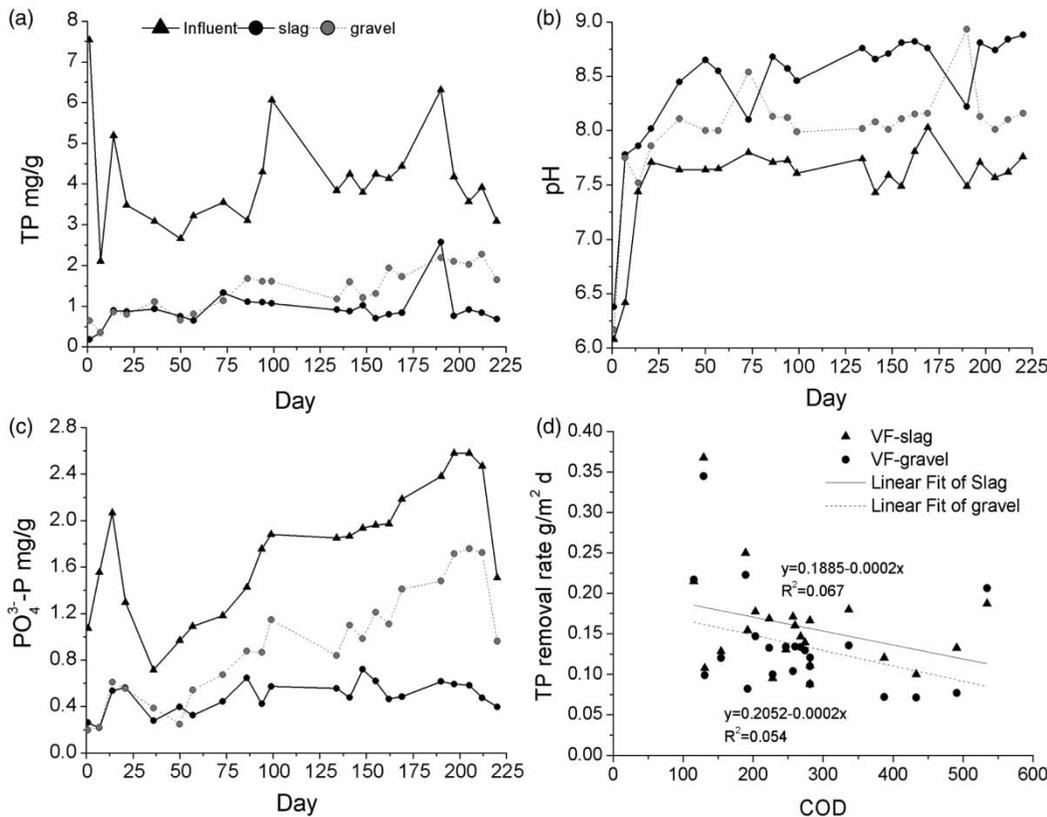


Figure 6 | Profiles of (a) TP, (b) $\text{PO}_4\text{-P}$, (c) pH at the influent and effluent, and (d) relation between influent COD and P load removal in the two VF CWs during the 220 days' operation.

The batch sorption study showed that the concentration of OM in solution had minimal effects on the P removal. This effect was slightly different for the laboratory-scale VF study, whereby the $\text{PO}_4\text{-P}$ removal rate showed a slight dip with the increase of the influent COD concentration (Figure 6(d)). Nonetheless, the overall influence of OM on P removal was not significant in the VF CWs, which is consistent with the findings from the sorption experiment. It has been noted that competitive interaction between anionic sorbates can occur directly through competition for surface sites and indirectly through effects of anion adsorption on surface charge and protonation (Huang *et al.* 2003).

Sorption of P is known to be a finite process. Thus, the slag is expected to be saturated with the continuous operation of the VF wetlands. According to the maximum sorption capacity of the slag (3.15 mg/g) and the saturated sorption capacity, which has been determined to be about 30–40% of the maximum sorption capacity (Drizo *et al.* 2002), the saturated sorption capacity of 0.95–1.26 mg/g is obtained. Therefore, with the total amount of slag in the VF system of 250 kg and the average influent P concentration of 4 mg/L, the VF system is expected to be saturated after about 11–15 years of operation. Therefore,

it may be necessary to replace the saturated slag substrates with fresh ones after this period.

CONCLUSIONS

The P removal performance of two VF CWs containing either steel slag or gravel substrates were evaluated. Isothermal sorption data were fitted to the Langmuir and Freundlich equations, which indicated sorption capacities of 3.15 mg/L and 0.81 mg/L, respectively, for slag and gravel. The kinetic equation fitting showed that the experimental data fitted better to the pseudo-second-order model ($R^2 > 0.99$) and that chemisorption was the rate controlling step. The four common types of OM played different roles in P sorption. Among these, citric acid inhibited the P sorption, whereas oxalic acid promoted the combination of P with metal ions. During a 220-day operation period, the VF-slag removed 76.0% of the influent TP at 0.159 g/m²·d and $\text{PO}_4\text{-P}$ of 70.9% at 0.063 g/m²·d, whereas the VF-gravel removed 65.0% at 0.136 g/m²·d and 48.6% at 0.040 g/m²·d, respectively. Thus, slag can significantly enhance $\text{PO}_4\text{-P}$ removal in VF CWs. With a saturated sorption capacity of

0.95–1.26 mg/g, the slag substrate is expected to be replaced after about 11–15 years.

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