Phosphorus Sorption Capacities of Steel Slag in Pilot-Scale Constructed Wetlands for Treating Urban Runoff: Saturation Potential and Longevity

W J Guo, L Y Zhao, W H Zhao, Q Y Li and Z B Wu

Abstract. Two parallel pilot-scale integrated constructed wetland (ICW) systems were constructed on the bank of Nanfeihe River. The phosphate (PO$_4^{3-}$) isothermal adsorption properties of the upper substrate steel furnace slag (SFS) in up-flow chamber was investigated during one-year operation period. The maximum phosphorus (P) adsorption capacity of SFS 9, 11, 13, 15, 17, 19 months service time were 848.9 mg/kg, 968.1 mg/kg, 824.5 mg/kg, 788.7 mg/kg, 864.7 mg/kg and 960.3 mg/kg, respectively. The saturated adsorption amount of SFS had not decreased with the service time prolonging in ICW. The longevity of a full-scale system could not be reliably estimated only based on the theoretical saturated adsorption capacity from laboratory experiments.

1. Introduction

Constructed wetlands (CWs) have been accepted as a new ecological engineering technology all over the world and were more widely used in developing countries where sewage collection and treatment facilities are poorer. CWs have been proved to be an effective way to treat domestic sewage, industrial wastewater and livestock wastewater. Furthermore, more studies and engineering practices have strongly approved that CWs could be used for non-point source pollution control.

It is generally believed that phosphorus (P) is one of the main control factors of water eutrophication that would be seriously exacerbated when the total P concentration in the water is...
greater than 0.02 mg/L [6]. It is of significantly important to alleviate water pollution and eutrophication by removing P pollutants effectively from the effluent. CWs have possessed many advantages of a low investment; convenient maintenance and outstanding ecological service function on removal and gradually become a new technology of wastewater treatment. In CWs, P in sewage was mainly removed by the adsorption and/or precipitation of substrates, bacterial activity, absorption of plant and algae and organic matter complexation [7]. The importance of substrates adsorption for removal by CWs has been recognized for nearly 3 decades.

However, it is worth noting that adsorption and/or precipitation of P by substrates in CWs is a finite process. Once the material becomes saturated, it will have to be either washed or replaced, or else P pollutants will be released and leads to water pollution [8]. Therefore, the P adsorption capacity of substrates represents a central parameter for comparing and selecting candidate materials to be used as key removal media in CWs [8,9]. Nevertheless, while acquiring the information of adsorption capacity of some candidate substrates can be used to estimate the maximum amount of P from the influent, it is difficult to provide an accurate estimation of the longevity of CWs. The longevity of CWs is restricted by the P saturation potential of the substrates as well as the feeding regime (e.g. hydraulic retention time, HRT), plant growth, microorganism activity and P concentrations of influent. Thus it is obvious that using the Langmuir equation with experimental data of laboratory test cannot obtain the realistic adsorption capacity of substrates in pilot-scale CWs and the longevity. It was recommended that P batch experiments should be coupled with a longer-term investigation of substrates performance through columns or even pilot-scale study for the better estimation of P removal efficiencies and retention capacities of different substrates. Therefore, it is necessary to carried out the study of the saturated adsorption capacity and variation tendency of substrates with the service time prolonging during based on pilot-scale CWs, which is of great benefit to predict the long-term performance and improve the purification capability of CWs.

In this study, two parallel pilot-scale integrated constructed wetland (ICW) systems were constructed on the bank of Nanfeihe River, a seriously polluted urban river, for purifying urban runoff. The detail operation and pollution removal efficiencies were performed in another paper [10]; here, we focused on the phosphate (PO$_4^{3-}$) isothermal adsorption properties (linear Langmuir equation) of the upper substrate Steel furnace slag (SFS) in up-flow chamber based the ICW in an operation period of one year. The maximum P adsorption capacity of SFS was also investigated with its service time prolonging in ICW. This long-term pilot-scale study was conducted to provide a theoretical basis for optimizing the purification performance and realizing the long-term operation of CWs.

2. Materials and methods

2.1. Site description and design of the ICW

Two parallel pilot-scale ICW systems (each was composed of a IVCW and HSSF-CW in series) were constructed on the bank of Nanfeihe River, a tributary and the biggest pollution source of Chaohu Lake, in Heifei, China. The ICW systems were constructed in early May 2011. Each was designed as a combination system of a down-flow chamber (DFC, 50 m$^2$ and planted with Canna indica), an
up-flow chamber, and a horizontal subsurface-flow chamber in series (Fig.1) (For more information, refer to Guo et al. [10]. This study mainly focused on the IVCW, especially the DFC, to explore the saturated adsorption capacity and variation tendency of SFS used in the chamber.

![Figure 1](image_url)

**Figure 1.** The down-flow chamber(A) and up-flow chamber(B) of the IVCW.

2.2. Operation conditions
The wastewater was pumped from the sedimentation tank in a pump station and induced in each ICW unit per day to yield a hydraulic loading rate of 100 mm/d, and the theoretical HRT was about 2.2 d [10].

2.3. Sampling and analysis
Five representative rhizosphere samples were collected from five target plants in DFC and homogenized well to make a composite sample once in every two months from mid-March 2012 to mid-January 2013. After all litter was removed, the field-moist samples were sieved with 10 mm separating sieve and dried at room temperature, then sealed in a desiccators for determination.

The maximum P adsorption capacity was determined using a slightly modified batch equilibrium technique as described by Drizo et al. [8,9]. The maximum P adsorption capacity was calculated from the difference between the initial P concentration added to the solution and the P concentration in the supernatant, using the nonlinear form of the Langmuir equation:

\[
\frac{C_e}{q} = \frac{C_e}{b} + \frac{1}{ab}
\]

where \(C_e\) is the concentration of P in the solution at equilibrium (mg/L), \(q\) is the amount of P adsorbed per unit mass of material (mg/g), \(b\) is the maximum P adsorption capacity (mg/g), and \(a\) is the constant related to the binding strength of P onto the material.

2.4. Statistical analysis
Statistical analyses were performed using SPSS13.0 for Windows (SPSS Inc., Chicago, IL, USA; Version 13.0). The experiment data were presented as mean ± standard deviation. Comparison of the averages was analyzed using one-way ANOVA followed by LSD tests.

3. Results and Discussion
In the research of adsorption kinetics, Langmuir formula and Freundlich formula, as two common isotherm equations, are often used to represent the adsorption process of different materials on pollutants. Wherein, Langmuir equation is constructed by Langmuir in 1961, and the original form is $q = abC_e/(1+aC_e)$. Several important parameters about adsorption characteristics, including $a$, $q$ and $b$ (see above), can be obtained according to this equation consequently that has been widely used in characterizing the adsorption processes of different medium on pollutants. When $a > 0$, the reaction between materials and pollutants at the same temperature conditions can occur spontaneously, and higher values indicate a stronger spontaneity degree and adsorption capacity on pollutants and more stable products.

If pollutant concentrations (i.e. initial P concentration in experiment) are relatively higher, the theoretical value calculated from fitting Langmuir equation could differ from the true value to a certain extent. Whereas, when the pollutant concentration is relatively lower, the equation could be capable of fitting the actual adsorption process [11]. Therefore, the maximum $PO_4^{3-}$ concentration (concentration gradient of $KH_2PO_4$ solution) in this study was set to 80 mg/L, simulating the actual adsorption process of the SFS as accurately as possible.

In the study, the Langmuir isotherm plot of P adsorption data for SFS collected from different dates (i.e. different service time) were shown in Figure 2. All the values of the correlation coefficients ($r$) estimated by Langmuir isotherm plot of SFS from different dates were greater than 0.9 and present the better fitting goodness. Therefore, the Langmuir model is suitable for simulating the isotherm plot of P adsorption for SFS of different service time.

The maximum P adsorption capacity ($b$) and binding energy constants ($a$) as estimated by Langmuir isotherm plot of SFS from different dates were illustrated in Table 1. The $b$ value of SFS from March 2012 (9 months of service time), May 2012 (11 months of service time), July 2012 (13 months of service time), September 2012 (15 months of service time), November 2012 (17 months of service time), January 2013 (19 months of service time) were 848.9 mg/kg, 968.1 mg/kg, 824.5 mg/kg,
788.7 mg/kg, 864.7 mg/kg and 960.3 mg/kg, respectively. Based on these results, it is concluded that the saturated adsorption amount of SFS have not decreased with the prolonging of service time in the pilot-scale ICW.

**Table 1.** Maximum P adsorption capacity (b), binding energy constants (a) and correlation coefficients (r) as estimated by Langmuir isotherm plot of SFS from different dates.

| SFS of different service time | Maximum P adsorption capacity, b (mg/kg) | Binding energy constants, a | Correlation coefficients, r |
|------------------------------|------------------------------------------|----------------------------|-----------------------------|
| Mar. 2012                    | 848.90                                    | 0.17                       | 0.9770**                   |
| May. 2012                    | 968.05                                    | 0.11                       | 0.9663**                   |
| Jul. 2012                    | 824.47                                    | 0.09                       | 0.9172**                   |
| Sep. 2012                    | 788.71                                    | 0.16                       | 0.9567**                   |
| Nov. 2012                    | 864.68                                    | 0.17                       | 0.9792**                   |
| Jan. 2013                    | 960.34                                    | 0.11                       | 0.9467**                   |

According to maximum P adsorption capacity obtained in the experiment, it could be expected to make a preliminary estimate for the life expectancy of SFS in ICW. The working life and durability of CWs is closely related to the concentration and type of pollutants in the influent.

Assuming the CWs possess a same removal rate whether under the high hydraulic loading rate (HLR) or low HLR, the theory service life of CWs could be calculated as follows. It is assumed that 2.3 g P per person per day were discharged in municipal wastewater. According to the wetland design guidelines (EC/EWPCA) described by Drizo et al. [9], a 3 m$^3$ wetland (wetland area is 5 m$^2$ and depth is 0.6 m) was required to constructed to purify the discharged sewage and about 4.5 tons SFS needed to be filled in the CWs. Applying the saturated adsorption capacity (the average value was 0.88 kg P, see Table 1) to the 3 m$^3$ wetland mentioned above, 4.5 ton SFS could remove 4.0 kg P and the life expectancy was about 9 years.

In CWs, P in the influent can make complexation with Fe, Al and Ca ion and be removed via adsorption and/or precipitation by substrates, which have been considered as the main way and mechanism for P removal [12]. The P maximum adsorption capacity and the longevity of substrates are two important parameters in the practical application of CWs. It was shown that the saturated adsorption capacity of SFS had not continued to decrease with the increase of its service time in wetland system after nearly a year research. The P adsorbed on the SFS surface can be removed to some extent by the absorption of plants, which may be one of the reasons for the substrates maintaining the adsorption longevity in CWs [13]. Furthermore, the ICW system was operated in an intermittent way and batch injection of the influent can maintain the environment in which the anaerobic and oxygen enrichment condition occurred alternately [14]. In this study, the P adsorption ability of SFS had been recovered to a certain degree at least in the short term.

**4. Conclusions**

In conclusion, the Langmuir model could be suitable for simulating the phosphorus adsorption isotherm of SFS, the maximum adsorption capacity of which had not continued to decrease with the
service time increase in ICW during operating period. Consequently, the longevity of a full-scale system could not be reliably estimated only based on the theoretical saturated adsorption capacity obtained by laboratory experiments. Besides, it was unreliable to take it as a central parameter for comparing and selecting candidate materials to be used as P removal media in CWs. The longevity of full-scale CWs should more reliably be evaluated from a P saturation value derived from a long-term column or pilot-scale study and that could provide useful data about the suitability of substrates in CWS for long-term P removal and the prediction of the longevity of the pilot-scale design.

Acknowledgement
The research was financially supported by National Natural Science Foundation of China (Grant No. 51509011) and Special fund for basic scientific research business of central public research institutes (Grant No. CKSF2016002/SH).

References
[1] Hadad H R, Maine M A and Bonetto C A 2006 Macrophyte growth in a pilot-scale constructed wetland for industrial wastewater treatment. *Chemosphere* 63(10): 1744-53.
[2] Cheng S, Grosse W, Karrenbrock F and Thoennessen M 2002 Efficiency of constructed wetlands in decontamination of water polluted by heavy metals. *Ecol. Eng.* 18(3): 317-325.
[3] Lai D Y F and Lam K C 2009 Phosphorus sorption by sediments in a subtropical constructed wetland receiving stormwater runoff. *Ecol. Eng.* 35(5): 735-743.
[4] Wu C Y, Kao C M, Lin C E, Chen C W and Lai Y C 2010 Using a constructed wetland for non-point source pollution control and river water quality purification: a case study in Taiwan. *Water Sci. Technol.*, 61(10): 2549-55.
[5] Maniquiz M C, Lee S Y, Choi J Y, Jeong S M and Kim L H 2012 Treatment performance of a constructed wetland during storm and non-storm events in Korea. *Water Sci. Technol.* 65(1): 119-126.
[6] Sallade Y E and Sims J T 1997 Phosphorus transformations in the sediments of Delaware's agricultural drainage ways: II. Effect of reducing conditions on phosphorus release. *Environ. Qual.* 26(6): 1579-88.
[7] Lantzke I R, Mitchell D S, Heritage A D and Sharma K P 1999 A model of factors controlling orthophosphate removal in planted vertical flow wetlands. *Ecol. Eng.* 12(1): 93-105.
[8] Drizo A, Comeau Y, Forget C and Chapuis, R P 2002 Phosphorus saturation potential: a parameter for estimating the longevity of constructed wetland systems. *Environ. Sci. Technol.* 36(21): 4642-48.
[9] Drizo A, Frost C A, Grace J and Smith K A 1999 Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Water Res.* 33 (17), 3595-3602.
[10] Guo W J, LiZ, ChengSP, LiangW and WuZB 2014 Performanceof a pilot-scale constructed wetland for stormwater runoff and domestic sewage treatment onthe bank of a polluted urban river, *Water Sci. Technol.* 69 (7): 1410-18.
[11] Li Q N, Zhang J Q, Xie J and Xu W L 2011 Performances and dynamics of substrate in constructed wetland system adsorbing phosphorus. *Tech. Water Treat.* 37(9): 64-67.

[12] Johansson L 1999 Blast furnace slag as phosphorus sorbents-column studies. *Sci.Total Environ.* 229(1): 89-97.

[13] Greenway M and Woolley A 1999 Constructed wetlands in Queensland: performance efficiency and nutrient bioaccumulation. *Ecol. Eng.* 12(1), 39-55.

[14] Shilton A, Pratt S, Drizo A, Mahmood B, Banker S, Billings L, Glenny S and Luo D 2005 Active filters for upgrading phosphorus removal from pond systems. *Water Sci. Technol.* 51(12): 111-116.