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Elimination of phosphorous from phosphorus-rich farmyard wastewater using reeds bed system containing steel furnace slag

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ABSTRACT

It has been demonstrated that blast furnace slag (BFS) has high P adsorption capacity. Steel furnace slag (SFS) has similar physical and chemical properties to BFS, but whether the former has similar P adsorption characteristics to the latter is unclear. In order to assess its reuse potential as main filter media in treating phosphorus-rich farmyard wastewater, the phosphorus adsorption isotherm of SFS in high-P solution was derived and the adsorption process was examined as a function of pH; then, SFS was used as a main substrate in a tidal flow reed bed system and its treatment performance was evaluated to determine the removal efficiency of COD, BOD_5, SS, TN and PO_4-P during farm wastewater treatment process. Compared with Freundlich and Tempkin isotherm, Langmuir model yielded the best fit for the SFS. The maximum adsorption capacity reached 27.8 mg P/g at an optimum pH of 4.0. Our results show that SFS reed bed may be a novel effective system to wipe off phosphorus from wastewater, and then it may also provide an approach for the reuse of SFS.

Keywords: Phosphorous adsorption; Steel furnace slag (SFS); Reed bed; Tidal flow

1. Introduction

Phosphorus enters the natural waters possibly from various fertilizers industries, domestic sewage, laundries or even phosphorus-rich rocks. Excessive amount of phosphorous in the water body can result in eutrophication. In water bodies with poor circulation, phosphate concentrations as low as 1 mg P/L is sufficient to stimulate algal blooms [1]. Therefore, a crucial issue is to adopt an effective method to remove P from wastewater before discharging, in order to meet the effluent limits of 0.5–1.0 mg P/L [2]. At present, reducing P levels in wastewater can be achieved by the various techniques, e.g. traditional chemical precipitation with aluminium, calcium and iron salts [3,4], various physico-chemical methods including reverse osmosis, electrodialysis, contact filtration and adsorption [4]. In these techniques, adsorption technology is regarded as more useful and economic for phosphorous removal, especially for low phosphorous concentration. However, expensive adsorbent will restrict the commercial application of this technology. So looking for a cheap and efficient adsorbent becomes a key to promotion of the technology.

In the past few decades, the removal of phosphate from wastewater using adsorption technique has been widely investigated by many researchers [5], which is based on various adsorbents such as oyster shell [6], recycled glass [7], recycling Fe(III)/Cr(III) hydroxide

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[8], mixed lanthanum/aluminium pillared montmorillonite [9], thermally treated natural palygorskite [10] and modified honeycomb cinders [11]. Steel slag, such as blast furnace slag (BFS) and steel furnace slag (SFS) is a by-product generated in the steel manufacturing process. It is usually used in the production of self-cementing, long-lasting paving materials and rail ballast for the purpose of recycling in most countries of the world. But in today's China, utilization ratio of steel slag still remains low because of the lack of its recycling technology. So, exploring new approaches to reuse steel slag is beneficial to improve composite technologies related to environmental protection and resource recovery. It has been demonstrated that BFS has high P adsorption capacity [12–14] in that calcium, aluminium and iron are dominant components, which contribute to P adsorption through ligand exchange and precipitant reaction [15]. SFS has similar physical and chemical properties to BFS, but whether the former has similar P adsorption characteristics to the latter is uncertain.

In order to examine P adsorption characteristics of SFS and explore the possibility of using SFS as a potential substrate for reed bed system, in this study, we have evaluated the P adsorption capacity of SFS under the condition of high-P solution in a batch experiment and then, in a tidal flow by using reed bed system using SFS as main substrate, we have examined the efficiency of pollutants removal, especially P removal during the treatment of high-P animal farmyard wastewater from rural areas.

2. Materials and methods

2.1. SFS collection and high-P solution preparation

SFS samples were collected from the Anyang Iron & Steel Group Co. Ltd., Henan Province, China. It was formed during the conversion of pig-iron to steel, a process that removes some impurities. After being ground, SFS was sieved into particles (Particle diameter is 200–300 μm). The major element components of SFS were determined by ICP analysis and listed in Table 1. The P stock solution was prepared in distilled water with potassium dihydrogen phosphate (KH_2PO_4). All working solutions were prepared by diluting the stock solution with distilled water.

2.2. Batch P adsorption experiment

In order to examine P adsorption, different 30 ml aqueous solution with different P concentration is equilibrated with 0.1 g particles (diameter 200–300 μm) of SFS, respectively, and then each suspension was transferred to the corresponding 150 ml plastic bottles, next, on a shaker, they were agitated at 150 rpm, 23℃ for 12 h to ensure equilibrium. At the same time, the pH values of the suspensions were adjusted to 2.0, 3.6, 4.0, 5.5, 8.0 and 10.5 by manually adding 0.5 N HNO_3 or 3 N NaOH. After 12 h of continuous shaking, the samples were filtered with a 0.45 μm MF-Millipore membrane filter to separate the solids from the liquids. The residual P concentration was determined according to molybdenum blue colorimetric method. In order to obtain the isotherm data, five levels of initial phosphate concentrations (12.5, 25, 50, 100, 200 mg P/L) were designed and all the samples were maintained at pH 4.0. The values are the average of replicate measurements.

2.3. Laboratory scale four stage tidal flow operation

Four stage CW systems were established based on the identical reed beds which were made of four Perspex columns with a length of 1,200 mm and a diameter of 100 mm. A schematic diagram of the systems used in the study is illustrated in Fig. 1. The systems are configured (from the top) with 100 mm soil as culture medium for plant growth. Immediately under the culture medium, 450 mm thick steel slag layer was laid and finally, 100 mm thick gravel layer was place at the bottom as the support matrix. The common reed, *Phragmites communis*, in Baiyangdian District, Hebei Province, China was planted on the top of each bed. Raw wastewater was collected from the Xinxiang Liangzhong animal farmyard located at Xinxiang City, Henan Province, China with about 4,200 livestock units mainly including pigs and cattle. Prior to treatment, the wastewater collected was settled in a 15 m^3 capacity tank. The supernatant was diluted with tap water and the diluted liquid was used for influent in this experiment of the CW systems. The flow rate of influent was 48 ml/min. The influent and effluent Samples of the systems were analysed for SS, COD, BOD_5, PO_4^{3-} and TN. The characteristics of the diluted animal farm wastewater are listed in Table 2. BOD_5 was determined using a BODTrak instrument (CAM-LAB Ltd., UK). PO_4^{3-} concentration was determined according to molybdenum blue colorimetric method. The remaining parameters were obtained according to "Standard Methods for the Examination of Water and Wastewater" (APHA, 1995).

3. Results and discussion

3.1. Adsorption isotherm

To assess the P adsorption potential of SFS, Langmuir, Freundlich and Tempkin isotherm were

Table 1
The principal chemical compositions of SFS

Chemical composition	Amount (%) SFS
Calcium (as CaO)	29.27
Iron (as Fe_2O_3)	26.43
Aluminium (as Al_2O_3)	4.79
Silicon (as SiO_2)	4.76
Manganese (MnO)	0.31
Moisture content	99.2

Table 2
Characteristics of the animal farm wastewater used in this study

Parameters	Values
SS (mg/L)	85–190
COD (mg/L)	212–358
BOD_5 (mg/L)	81–230
TN (mg/L)	225–350
Phosphorus (PO_4^{3-}) (mg/L)	51–95
pH	7.4–8.4

used for fitting the adsorption equilibrium data. The linear forms of Langmuir's isotherm model, Eq. (1), Freundlich's model, Eq. (2), and Tempkin model are given in the linear forms of:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (1)$$

$$\log q_e = \log K_d + (1/n) \log C_e \quad (2)$$

$$q_e = B \ln A + B \ln C_e \quad (3)$$

where q_e is defined as before (mg P/g), b (L/mg) a adsorption constant relative to P binding energy, Q_0 the maximum adsorption capacity (mg P/g steel slag) and C_e is the equilibrium P concentration (mg P/L steel slag). The slope and the intercept of the plot of (C_e/q_e) vs. C_e give the values of Q_0 and b. K_d is the distribution coefficient and n is a correction factor of the Freundlich model. B and A are the Tempkin constants and can be determined by a plot of q_e vs. ln C_e.

The theoretical parameters of isotherms along with correlation coefficient and S.D are listed in Table 3. It is clear that the experimental data of P adsorption onto SFS could be well fitted by the three models. Relatively, Langmuir isotherm exhibited a better fit than Freundlich and Tempkin isotherm, which is

Table 3
Langmuir, Freundlich and Tempkin isotherm parameters for P removal by SFS under pH 4.0

Langmuir equation:	$C_e/q_e = 1/Q_0b + C_e/Q_0$	R	S.D
Q_0(mg P/g)	b		
24.44	0.188	0.994	0.26
Freundlich equation:	$q_e = K_F C_e^{1/n}$	R	S.D
K_F	1/n		
6.56	0.282	0.977	0.079
Temkin equation:	$q_e = A + B\ln C_e$	R	S.D
A	B		
7.767	3.08	0.989	1.377

agreed with the recent results reported by Jie et al. [16] in a similar study. The value of Q_0 is compared among the similar systems with different adsorbents, such as hematite (3 mg/g P) [17], furnace slag (0.65 mg/g P) [12] and recycling (III)/Cr (III) hydroxide (6.5 mg/g P) [8]. Comparative value of Q_0 (24.4 mg/g) indicates the potential application of steel slag as an effective adsorbent for P. As shown in Table 1, the amount of calcium, iron and aluminium (expressed as oxidized metal) in the SFS was 29.27, 26.43 and 4.79%, which are related to P-metal adsorption and/or precipitation. Thus, it is reasonable to conclude that SFS has the considerable high P adsorption capacity.

3.2. Effect of pH

The effect of pH on the P adsorption of steel slag is presented in Fig. 2. As shown in Fig. 2, the optimum pH is 4.0 at which the amount of P adsorption of steel slag was 27.8 mg P/g, while at pH 10.5, this amount reached a minimum of 4.3 mg P/g. The results indicate that the P adsorption of steel slag is a physico-chemical process and that the P adsorption ability is strongly dependent upon the pH of solution. This suggests that acidic environment should be conducive to the absorption of phosphorus of steel slag.

3.3. Constructed vertical-flow reed bed wetland using steel slag as partial substrate

The reed bed system was fed by the animal farm wastewater from the 1st stage to 4th stage through a "tidal flow" strategy in which the "tide", namely the rhythmical filling and draining of the bed medium, was generated (in each stage) with a peristaltic pump controlled by a timer. The optimal conditions system of "tidal flow" under the system was a cycle of 4 h, which includes 1 h of wastewater-bed matrix contact

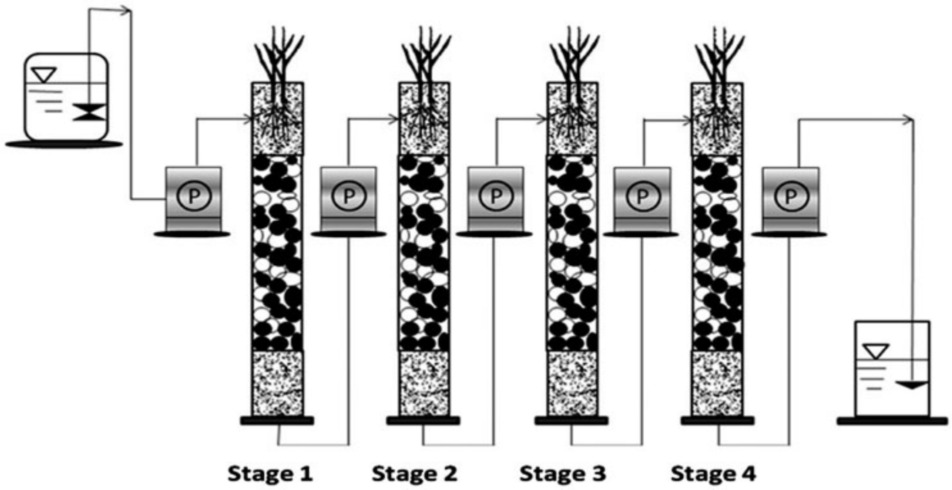

Fig. 1. The schematic of experimental reed beds system using SFS as main filter media.

and 3 h of resting. Compared with the traditional CW systems, it has been proved that the design of tidal flow is more beneficial since this system not only overcomes poor water distribution problem, but also enhances the oxygen mass transfer and diffusion from the open air into the reed beds [18,19]. However, the tidal flow reed bed system will increase the cost of wastewater treatment because it requires additional energy and equipments.

Each set of samples was taken after three operations to ensure access to the data under stable conditions. The level of COD and BOD_5 at the influent and effluent of the system is illustrated in Fig. 3. The average removal percentage of 89.8% for COD and 81.7% for BOD_5 was achieved. The value of COD removal is higher than that obtained from a constructed wetland with BFS substrate for treatment of domestic wastewater [20]. Because the COD level of farmyard wastewater is usually significantly higher than that of domestic wastewater, this may partially result in a higher COD removal efficiency in this study than in the previous study. The higher COD removal efficiency can be explained by the fact that higher amount of oxygen provided by the tidal flow can effectively enhance organic removal capacity of microorganisms in the filter media or the vegetative organ surfaces of macrophytes. What is more, Fig. 3 also illustrates the alteration of pH during the whole treatment process. At the early stage of the experiment, the pH in the system obviously became low, which likely results from the hydrolysis of SFS because once SFS contacted with wastewater, the H^+ ions would released into the effluent. After a 120-day operation, the pH in the system slightly reduces, which might be attributed to the formation of dissolved CO_2 and H_2CO_3 in effluent due to the degradation of organic compounds resulting from the progressively and complicatedly biological process inside the substrate [21]. Furthermore, the reeds might result in the decrease of pH through H^+ excretion, and this excretion is implemented through the organic acids exudation and CO_2 release from the root respiration resulting from the root cation exchange [22].

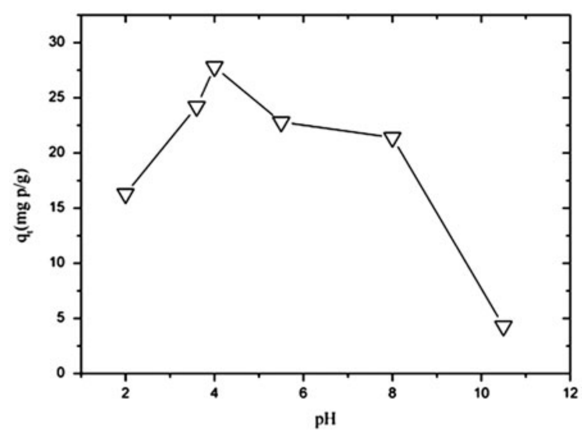

Fig. 2. Effect of pH on P adsorption onto SFS ($C_0 = 3{,}425$ mg/L, $T = 23$°C).

The SS, P and TN removal rate of the system are shown in Fig. 4. It is shown that the system has high phosphorus removal efficiency and that the average over 90% PO_4-P in the influent was consistently removed during one-year operation. It is demonstrated that SFS likely plays a crucial role in effectively removing phosphorous from wastewater through the adsorption/precipitant process. It is

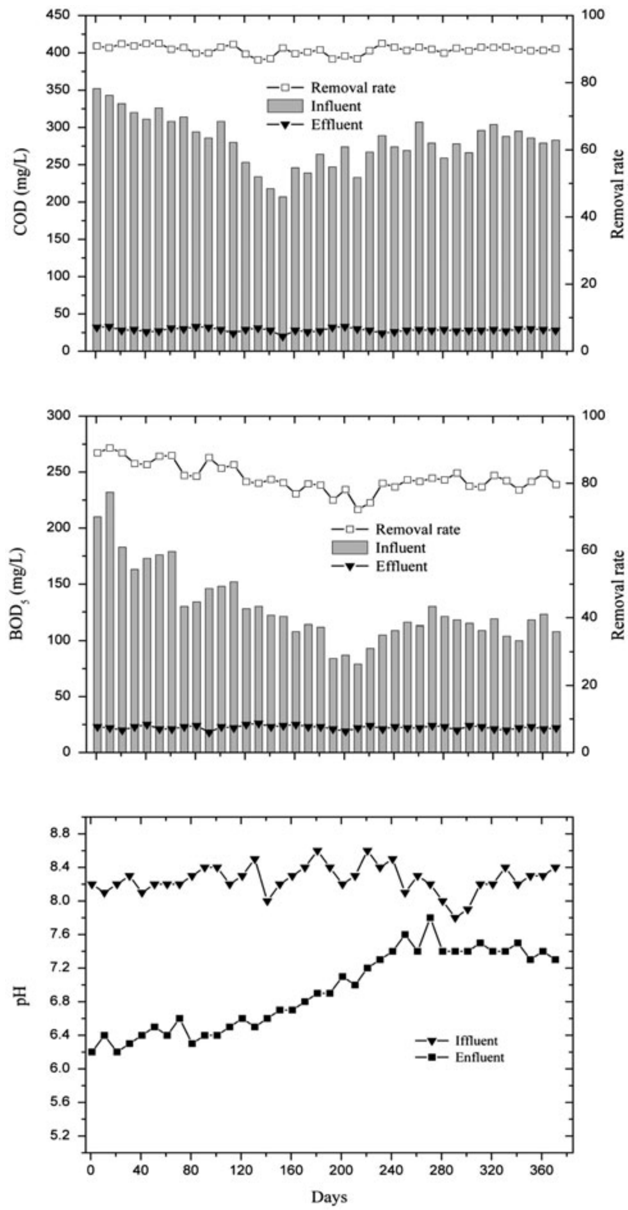

Fig. 3. Variations in BOD5 and COD in pH measurement for tidal flow.

interesting that the phosphorus removal efficiency of the system did not seem to be correlated to the pH value alteration during the monitored period. However, based on Fig. 2, when the pH value in the influent was greater than 4.0, the value of phosphorus removal rate should be inversely proportional to that of influent pH. It is suggested that other factors such as tidal flow strategy and other substrates might also play important roles in phosphorus elimination from wastewater, which likely reduced the correlation between phosphorus removal rate and pH value in the influent in the system. The average removal of TN, as shown in Fig. 4, is 78.8% and the higher removal efficiency may be contributed to oxygen supply in the four-stage CW system. It is possible that the sufficient dissolved oxygen resulting from tidal flow operation could promote nitrification in the treatment system. The average removal of SS is 83.4%, as shown in Fig. 4. In the system, it is believed that the filtration and the physical trap of the particles from SFS may be responsible for the high SS removal efficiency. Here, it has been demonstrated that the first stage of the

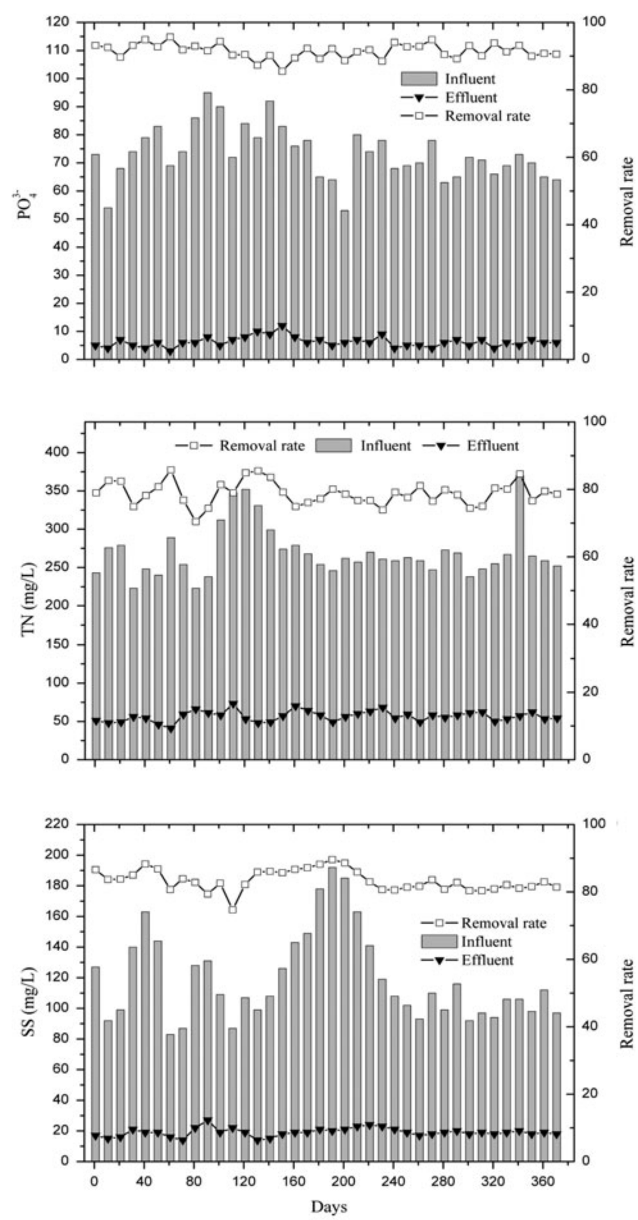

Fig. 4. Variations in PO_4^3, TN and SS measurement for tidal flow.

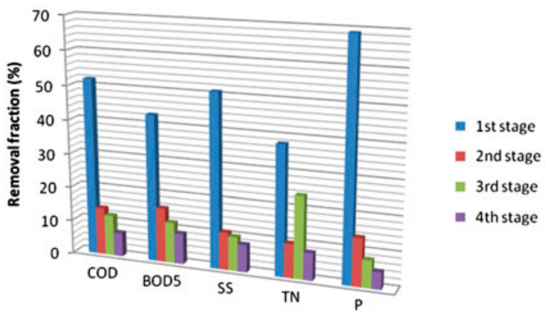

Fig. 5. Removals in individual stages of the tidal flow system.

system plays a key role in the COD, BOD_5, SS and PO_4-P removal (Fig. 5) in that, during this stage, 60% of the total COD removal, 57% of the total BOD_5 removal, 65% of the total SS removal and 75% of the total PO_4-P removal were achieved. At the first stage, the main reason for the high removal efficiency mentioned above might be due to the high retention of solids which may contribute to a merely apparent removal of COD, N and P. This retention is a short-term effect. In addition, when the raw wastewater flows through the column, not only can SFS absorb these pollutants, but the microorganism of the biofilms attached on the SFS can decompose the pollutants. The adsorption and decomposition take on a long-term effect. At the later stage of the trial, a higher TN removal efficiency appears to be observed suggesting that an active denitrification process may occur at this stage which is contrary to the active nitrification process at the early stage. Although the influent in the later stage has a relatively lower COD, plant root exudates may provide alternate organic carbon for denitrifying bacteria [23]. Further works need to examine the changes of NH_4^+-N, NO_3^--N and NO_2^--N in the whole process.

4. Conclusion

This study shows that SFS is an effective adsorbent for the removal of phosphorous from aqueous solution. Equilibrium adsorption data for P on SFS were well described by Langmuir model. Maximum P removal occurred during pH-related absorbent trials. In the constructed tidal flow reed bed system with the SFS as the main media, COD, BOD_5, TN, SS, especially PO_4-P can be efficiently removed from high P farmyard wastewater. The first stage of the systems plays the crucial role in removing carbonaceous and PO_4-P substrates. The remaining stages do not seem to exhibit significant difference in the removal efficiency of pollutants. Therefore, it is reasonable that SFS can be reused as a potential substrate material in reed bed treatment to efficiently remove P and other pollutions from wastewater. However, due to time and scale limitations in the study, more investigation will need to be carried out including studies on a larger scale and during a longer period.

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