



Converter slag–coal cinder columns for the removal of phosphorous and other pollutants

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ABSTRACT

A mixture of converter slag and coal cinder as adsorbent for the removal of phosphorous and other pollutants was studied in the paper. The maximum P adsorption capacity, pH of solution, contact time and initial phosphate concentration were evaluated in batch experiments for the two materials firstly. The data of P sorption were best fitted to Langumir equation, and the maximum adsorption capacities of converter slag and coal cinder were 2.417 and 0.398 mg P/g, respectively. The pH of solutions with converter slag and coal cinder changed dramatically with time and closed to 8 in 8 h, and the influence of initial pH on phosphate removal by coal cinder was more significant than by converter slag. Phosphate removal rate by converter slag decreased with increase of initial phosphate concentrations. Subsequently, two flow-through columns (Column 1#, $V_{\text{converter slag}}:V_{\text{coal cinder}} = 1:5$; Column 2#, $V_{\text{converter slag}}:V_{\text{coal cinder}} = 1:3$) were operated for the removal of phosphorous and other pollutants from the effluents of a vermifilter for nearly eleven months. Results indicated the average removal efficiency of total phosphorus, dissolved phosphorus, COD and NH_4^+-N by Column 1# were 44%, 56%, 31% and 67%, and by Column 2# were 42%, 54%, 24% and 57%, respectively. Column 1# had higher removal efficiency for P and other pollutants.

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1. Introduction

Onsite systems using media filters for wastewater treatment represent a viable alternative to conventional treatment and are of particular interest for small communities and rural areas in recent years [1,2]. A number of reactive substrates that may be appropriate filter media have been shown to efficiently reduce phosphorus (P) concentrations in the effluents [3–9].

Slag materials, e.g. blast furnace slag (BFS), electric arc furnace slag (EAF), and converter steel slag are the by-products from steel industries. Due to the main compositions of Fe- and Ca-oxides, they have been undergone the largest investigations for phosphorus removal [10–14]. Among the slag materials, converter slag had competitive advantages as the seed crystals for phosphorous crystallization, and it was also used as adsorbents for heavy metal removal in terms of its cost-effectiveness and high performance [12–14]. Many researches on using converter slag for the removal of phosphorous from wastewater have also been reported in China [15–17]. The mechanisms of phosphate removal by converter slag include the process of adsorption and precipitation, and the major mechanism is often determined by many factors, such as the chemical composition of the converter slag used and the

solution pH. There are a lot of studies focused on using converter slag as an adsorbent for phosphorus removal, however, in some column tests [15,17,18], it was found converter slag could easily aggregate together in water phase or moisture conditions. That made the hydraulic conductivities of the column decreasing, and treatment efficiency decreasing finally in concomitance with clogging. Other adsorbents based on iron oxides for P-removal were also found the clogging phenomena in column tests [19,20]. Sand had been mixed with such slags to avoid clogging, and the phosphorus removal rate can also be maintained at a good level for a short time [19,21]. However, to select substrates with conducive physico-chemical properties to P-removal, while maintaining sufficient permeability is of utmost importance for infiltration systems. Apparently, sand is not an appropriate substrate due to its finer texture and stable physico-chemical properties [22]. Few attempts are tried to resolve these problems in column tests and keep steady phosphorous removal rate in long run and simultaneously remove organic matter and ammonia from wastewater. A mixture of coal cinder and convert slag as column media will be an approach.

Coal cinder is an inorganic waste produced in coal combustion. It is a relatively coarse, gritty material and has a particle size generally within the range of 0.1–10 mm. Major constituents of coal cinder include silicone (Si), aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), potassium (K), sodium (Na) and titanium (Ti), which contents vary greatly depending on the coal type, source, and burning conditions. Zhang and Lei [23] used some of these con-

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Table 1
Property and composition of the converter slag and coal cinder.

Property and composition	Converter slag	Coal cinder
pH	10.31	8.50
Particle size (mm)	4.00–8.00	5.00–10.00
Particle density (g/cm ³)	3.77	2.01
Bulk density (g/cm ³)	1.58	0.64
Porosity (%)	34.41	68.25
FeO (%)	39.31	5.10
CaO (%)	28.43	4.50
SiO ₂ (%)	15.77	47.20
Al ₂ O ₃ (%)	2.31	36.10
MgO (%)	7.84	0.40
C (%)	–	4.30

stituents (Ca, Fe, or Al iron) to precipitate soluble phosphorus to reduce eutrophication of surface water. Due to the complex porous structure and higher hydraulic conductivity, coal cinder is often mixed with other materials, e.g. red clay, in soil treatment systems for improving the permeability and enhancing nitrogen removal [24,25]. It can also be used to immobilize cells or as filter media for advanced wastewater treatment [26] because of the high specific surface for microbial attachment and growth. However, coal cinder is prone to break down and clog, and it is often used as an additive in filter media. The mixture of coal cinder and converter slag as filter media for wastewater treatment could not only exert the higher phosphorous removal ability of converter slag, but also improve the effluent quality by removing ammonium nitrogen and organic matter. Moreover, converter slag and coal cinder are staple solid wastes in China and their utilization is also make sense to waste reuse.

The objective of this work was to test the feasibility of the mixture of converter slag and coal cinder as adsorbent for the removal of phosphorous and simultaneously advanced wastewater treatment. The advanced wastewater treatment considered in the study was specifically referred to remove COD and ammonia from the domestic wastewater. The maximum P adsorption capacity, solution pH, contact time and initial phosphate concentration of converter slag and coal cinder were evaluated in batch experiments using orthophosphate solution. Subsequently, two columns with different volume ratio of converter slag to coal cinder were conducted with effluents from a vermifilter. Total phosphorus and dissolved phosphorus, COD and NH₄⁺-N removal were investigated and an optimum mixture ratio of converter slag and coal cinder in the columns for wastewater treatment was performed.

2. Materials and methods

2.1. Materials

The converter slag used in the experiments was supplied by Baosteel Co., Ltd., Shanghai, China. It was screened between 4 and 8 mm. The coal cinder was obtained from the boiler house of Tongji University, and the particle size was between 5 and 10 mm. The property and composition of these materials were presented in Table 1.

2.2. Batch phosphate sorption experiments

The maximum phosphate adsorption capacity was determined using a slightly modified batch equilibrium technique [27] as described below. Nine P solutions, ranging from 2 to 200 mg P/L (2, 10, 15, 20, 40, 60, 80, 150 and 200 mg P/L, using KH₂PO₄ as P source) for converter slag; and ten P solutions, ranging from 2 to 80 mg P/L (2, 4, 6, 8, 10, 15, 20, 40, 60 and 80 mg P/L, using KH₂PO₄ as P source) for coal cinder were tested. The pH was maintained at 7.0 in all solutions. 5 g converter slag or 10 g coal cinder was put in

Table 2
Composition of the wastewater.

Composition	Wastewater from WWTP	Effluent from vermifiltration
COD (mg/L)	258.04 ± 7.80%	72.83 ± 5.31%
BOD ₅ (mg/L)	102 ± 4.53%	14 ± 2.11%
SS (mg/L)	138.36 ± 9.54%	15.78 ± 6.14%
DP (mg/L)	2.28 ± 7.34%	2.56 ± 4.99%
TP (mg/L)	3.55 ± 3.69%	2.96 ± 6.82%
TN (mg/L)	28.34 ± 7.63%	21.46 ± 9.15%
NH ₄ ⁺ -N (mg/L)	18.61 ± 2.33%	7.81 ± 5.88%

COD, BOD₅ and SS relevant chemical oxygen chemical. Five-day biological oxygen demand and suspended indicate DP and TP represent developed phosphorous; TN and NH₄⁺-N represent total ammonium nitrogen.

each 250 mL glass Erlenmeyer flask containing 100 mL of different P solution. These flasks were continuously shaken at 150 rpm on a sway gyratory shaker (DKY-II, Duke, China) for 48 h at 25 °C.

Different solution pH (initial values ranging from 3.03 to 11.02) and phosphate removal as a function with time were examined in a series of experiments using the same initial phosphate concentration of 20 mg/L, and the solutions were adjusted to the desired pH levels by using 0.1 mol/L HCl or NaOH solution. 5 g converter slag or 10 g coal cinder was put in each 250 mL glass Erlenmeyer flasks containing 100 mL of different P solution, and shaken at 150 rpm and 25 °C. At different time, the pH and phosphate concentration of the solution were measured.

The effects of initial phosphate concentrations (20, 40 and 60 mg/L phosphate solution for converter slag and 10, 20 and 30 mg/L phosphate solution for coal cinder) on phosphate removal were also investigated. The batch experiments were carried out using 5 g converter slag (10 g coal cinder) in 100 mL phosphate solution under above similar conditions, and the pH was also maintained at 7.0.

2.3. Removal of phosphate from a vermifilter effluent

Column adsorption tests on phosphate removal were conducted at room temperature using effluent from a vermifiltration system. Vermifiltration (or lumbrifiltration) is a new technology to process organically polluted water using earthworms. It was first advocated by the late Prof. Jose Toha at the University of Chile in 1992 [28,29] and now has been given more and more attentions due to the cost saving and ecologic characteristics [30,31]. The influent of the vermifilter was taken from a grit chamber of Shanghai Quyang wastewater treatment plant (WWTP). The compositions of influent and effluent from the vermifilter were shown in Table 2.

Two columns were constructed of PVC tubes of 50 cm length and 15 cm inner diameter and filled with a 35 cm layer of the appropriate filter material. The bottom of the columns was filled with a 5 cm layer of gravel to prevent loss of material from the columns. Considering the different phosphorous removal capacities of converter slag and coal cinder and simultaneous COD and NH₄⁺-N removal, the volume ratio of converter slag to coal cinder was tested in the experiments. Column 1# was designed as $V_{\text{converter slag}}:V_{\text{coal cinder}} = 1:5$, and Column 2# was designed as $V_{\text{converter slag}}:V_{\text{coal cinder}} = 1:3$. During the tests, the effluent from the vermifilter was collected in a storage tank and then continuously pumped to each column by peristaltic pumps at a flow rate of 200 mL/min. The effluent samples were collected daily for DP, TP, COD and NH₄⁺-N analysis.

2.4. Analytical methods

Chemical compositions of the converter slag and coal cinder were measured by atomic absorption spectrometry (AA-6501F, SHI-

MADZU, Japan). The pH values of converter slag and coal cinder were measured in their solutions with the solid/liquid ratio of 1:1. Solution pH was measured using a pH meter (pH 340i, WTW, Germany). A UV/visible spectrophotometer (S-2100, Shinco, Korea) was used to determine the concentrations of phosphorous and ammonia according to the standard methods [32]. COD was measured by a COD analyzer (NOVA 60, Merck, Germany). The changes of physico-chemical structure of the converter slag and coal cinder before and after column tests were determined using scanning electron micrograph (SEM). All sorption experiments were conducted in triplicates and the data were expressed as the average value.

3. Results and discussion

3.1. Chemical characteristics of the materials

The chemical composition of the materials for this study was presented in Table 1. The converter slag was rich in Fe- and Ca-oxides, representing 39.31% and 28.43%, respectively (Table 1). The metal oxides contents of converter slag in the study of Kim et al. [12] were Fe₂O₃ 25.9% and CaO 40.5%, respectively. It can be attributed to the different raw material and method of production. But comparing with the contents of BFS [5,10], both of the two converter slag have more Fe-oxides contents. Fe and Ca are known to play an important role in P retention by soils and sediments [33,34]. Phosphate ions react with iron oxides by ligand exchange forming inner-sphere complexes. The presence of Ca facilitates P retention via precipitation, and formation of Ca–P deposition on the solids surfaces [35]. Depending on the pH and the solution composition of Ca and P (H₂PO₄⁻ or HPO₄²⁻), several Ca–P may form: amorphous calcium phosphate (ACPs), octacalcium phosphate (OCP), dicalcium

Table 3
Langmuir and Freundlich isotherm parameters.

Parameters	Converter slag	Coal cinder
Langmuir	$Ce/qe = 1/bQ_m + Ce/Q_m$	
Q_m (mg P/g)	2.417	0.398
b (L/mg P)	0.266	0.113
R^2	0.992	0.914
Freundlich	$qe = KCe^{1/n}$	
K	0.402	0.052
n	1.856	1.975
R^2	0.739	0.891

phosphate (DCP), dicalcium phosphate dihydrate (DCPD), tricalcium phosphate (TCP) and hydroxyapatite (HAP) [36,37].

Al-, Fe- and Ca-oxides constituted 36.10%, 5.10% and 4.50% of the coal cinder, respectively (Table 1). The ingredient of Al is also effective for phosphate removal by ligand exchange [38]. The coal cinder was also high in Si, however, it was previously reported that Si has little efficiency for P retention [5]. The chemical contents of the coal cinder were very similar with fly ashes having low calcium contents [38].

3.2. Maximum P adsorption capacity

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The estimated model parameters with the correlation coefficient (R^2) for both Langmuir and Freundlich models are shown in Table 3. Both equations were suitable for the description of P sorption isotherm by converter slag and coal cinder, but the Langmuir equation was fitter

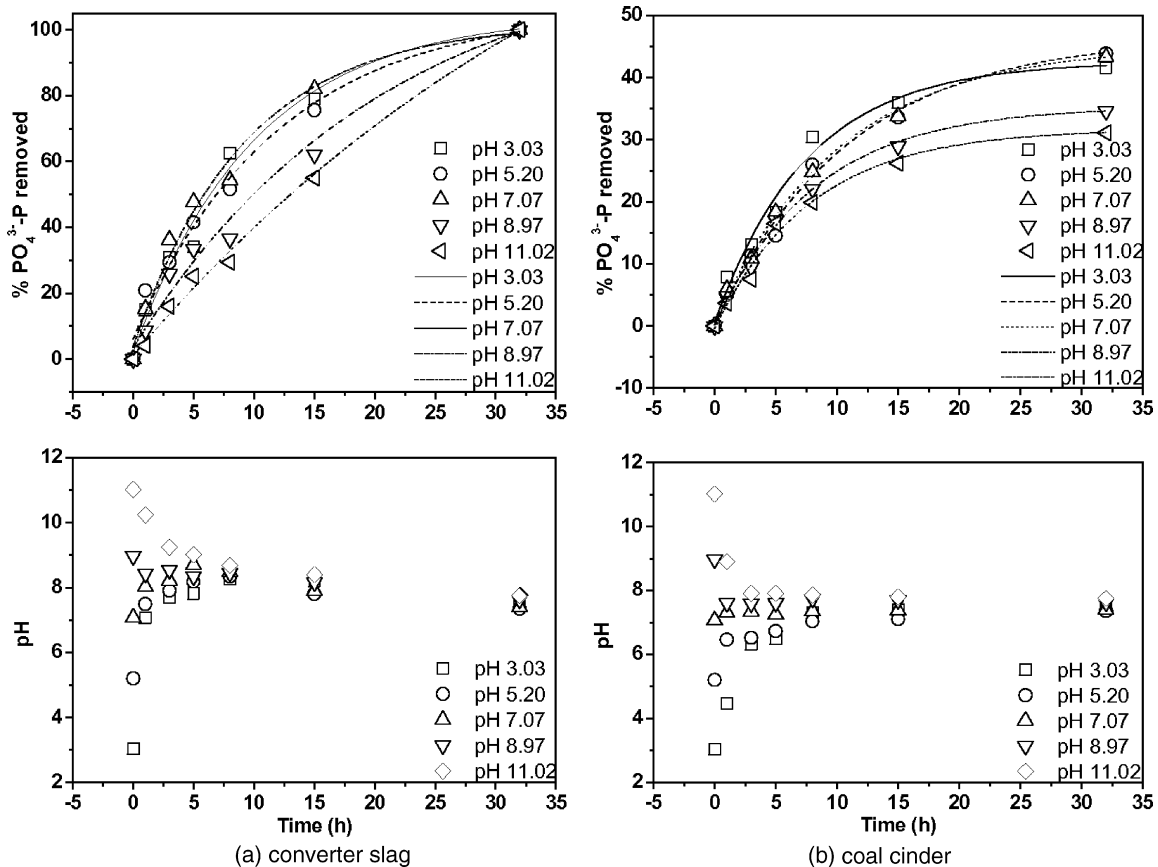


Fig. 1. Phosphate removal rates and solution pH changes with times by converter slag and coal cinder.

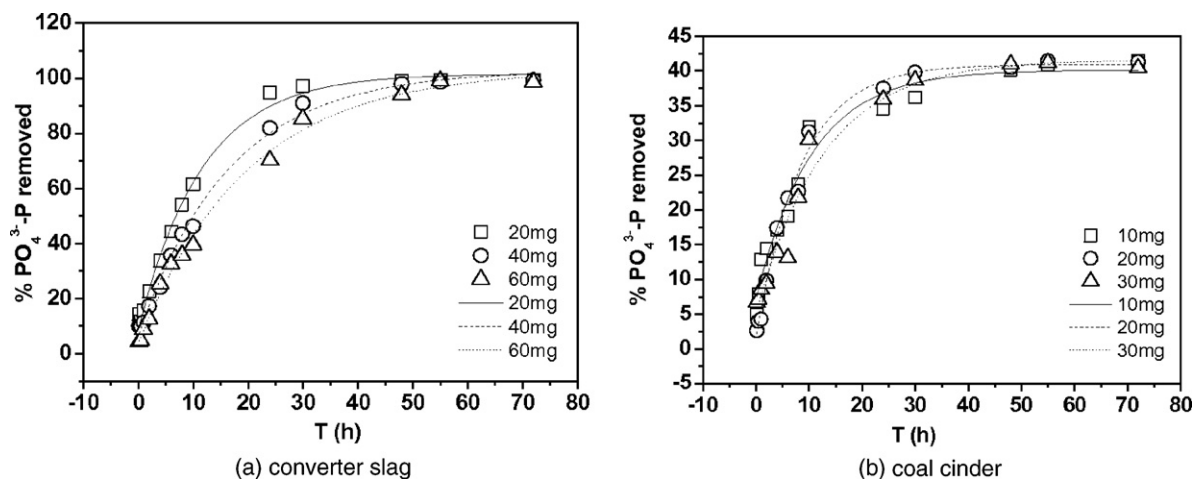


Fig. 2. Influence of initial phosphate concentration on phosphate removal by converter slag and coal cinder.

than the Freundlich equation according to the correlation coefficients (R^2). According to the coefficients of Langmuir isotherm the maximum adsorption capacity of converter slag was 2.417 mg P/g, and that of coal cinder was only 0.398 mg P/g.

The Langmuir and Freundlich parameters of converter slag could be compared with other sorbents based on metal oxides/hydroxides from literatures. Zeng et al. [19] reported that the values of Q_m , b , k and n for the P sorption on iron oxide tailing were 8.21 mg/g, 0.444, 3.59 L/g and 5.263, respectively. Xiong et al. [39] investigated P sorption capacities of steel slag through magnetic separation and obtained Q_m , b , k and n of 5.3 mg/g, 0.015, 0.088 L/g and 1.117, respectively. The sorption capacities of blast furnace slags varied from 0.65 to 44.2 g P/kg even with very similar chemical compositions [40]. Since there are many factors affecting P adsorption capacities of materials in batch studies such as the material used, the particle size, the period and temperature of contact between material and solution, the solution pH, the solution: material ratio, and the range of the initial P concentrations, and so on, the phosphorus adsorption capacities of materials derived from batch experiments can vary by several orders of magnitude.

3.3. Solution pH and P-removal varied with time

Solution pH plays a critical role in the rate and mechanism of the removal of phosphate. Five solutions with a same initial phosphate concentration (20 mg/L) and different initial solution pH values, in range of 3.03–11.02, were detected at different time intervals for converter slag and coal cinder, respectively. The results were shown in Fig. 1. It was found that even great differences existed in the initial pH; the solution pH would change dramatically and close to the neutral level with time, and then keep stable around pH of 8 in 8 h. The adsorption process, in which converter slag was used, started in the acid range and was followed by an increase of pH. The increase of pH was considered to be due to the slag dissolution, when some of the slag compound as iron, hydroxide and oxidehydroxide will be released to solution [41]. The decreasing of pH in basic range for converter slag can be explained that the removal of phosphate was accompanied by a decrease in the Ca^{2+} ion concentration and pH value [38]. Because Ca-, Fe- and Al-oxides contents also existed in coal cinder, it was found the same pH variety directions in the experiments of coal cinder.

The influence of initial pH on P-removal by converter slag was significant at beginning, and with solution pH closing to a stable value, the pH term was eliminated. The influence of initial pH

on phosphate removal by coal cinder was significant, especially in the terminal, and Fig. 1(b) showed that the initial pH ranging in 3.03–7.07 had a higher P-removal efficiency than the initial pH in basic range. The phosphate removal of the two materials tended to decrease with increasing initial pH above neutral. It is known that high pH and high Ca^{2+} concentration are advantageous for calcium phosphate precipitation; on the contrary, Fe- and Al-related components can play an important role in phosphate immobilization at acidic conditions [38]. Based on the chemical composition of the converter slag and coal cinder and the appropriate solution pH, it was believed that Fe content and Ca content contributed primarily to P immobilization in converter slag, and Al content contributed primarily to P immobilization in coal cinder. The mechanism of calcium contents in phosphate immobilization may be the formation of calcium phosphate precipitation by the reaction of dissolved Ca^{2+} with the phosphate in solution. The possible mechanism of iron oxide and aluminum oxide for the removal of phosphate can be explained by adsorption process through the ligand exchange between phosphate and the hydroxide groups on the surface of the hydroxylated oxides.

Fig. 1 showed the phosphate removal rate of converter slag was nearly 100% in 35 h, and the phosphate removal rate of coal cinder was 40% in 35 h. The different P-removal rate of the two materials can be attributed to the different P-removal mechanisms. Due to the higher Fe- and Ca-oxides in the converter slag while higher Al-oxides in the coal cinder (Table 1), the dominant mechanisms of P-removal by converter slag may be the adsorption and precipitation and by coal cinder may be mainly the adsorption.

3.4. Effect of initial phosphate concentration

The effect of varying initial phosphate concentrations on phosphate removal by the two materials was shown in Fig. 2. In Fig. 2(a), it was indicated the phosphate adsorption percentage increased with increasing contact time and attained equilibrium at variable time according to the initial concentrations of phosphate. It was more efficient for removing phosphate from dilute solutions than from concentrated solutions. In 24 h, the removal rate for initial phosphate 20, 40 and 60 mg/L was 94.88%, 81.98% and 70.25%, respectively. The results were similar with P adsorption by steel slag [39] and nickel adsorption by converter slag [14]. Fig. 2(b) showed the influence of initial phosphate concentration on P-removal rate by coal cinder was not as obvious as by converter slag due to the low P adsorption capacity of coal cinder.

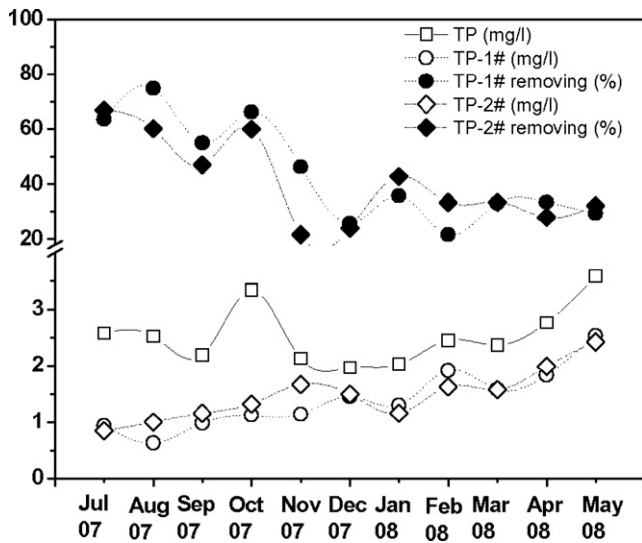


Fig. 3. TP removal from a vermifilter effluents through converter clog and coal cinder columns.

3.5. Removal of phosphate from the vermifilter effluent

Two columns flow-through adsorption tests were conducted for 319 days using the effluent from a vermifilter. The influent pH was maintained in range of 7.03–7.62 with a corresponding effluent pH of 7.11–8.19 during the test. The TP and DP concentrations of every month were shown in Figs. 3 and 4. The figures showed both TP and DP after the columns were largely reduced comparing to their influent concentrations. The reduction of TP was caused by infiltration removal of particulate P (PP) through the filter layer. The decrease of DP was mainly attributed to the phosphate adsorption on the substrates. The constant effluent concentration of the converter slag–coal cinder columns at the beginning of operation were mainly due to the higher P sorption capacity, when the adsorbent mixture was fresh and the sorption sites were free for P. Column 1# had higher TP and DP removal efficiency than Column 2# in first five months, although higher amount of converter slag were added in Column 2#. It was because fractional adsorption was dependent on phosphate contents taken by the influent at the initial time when the amount of converter slag was sufficient for adsorption. With

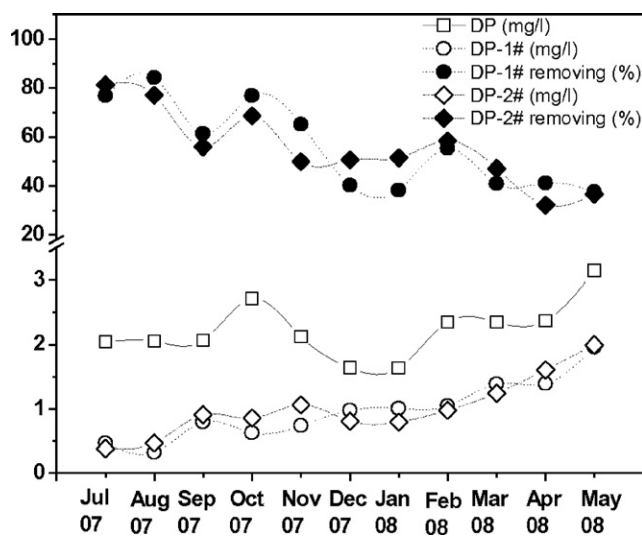


Fig. 4. DP removal from a vermifilter effluents through converter clog and coal cinder columns.

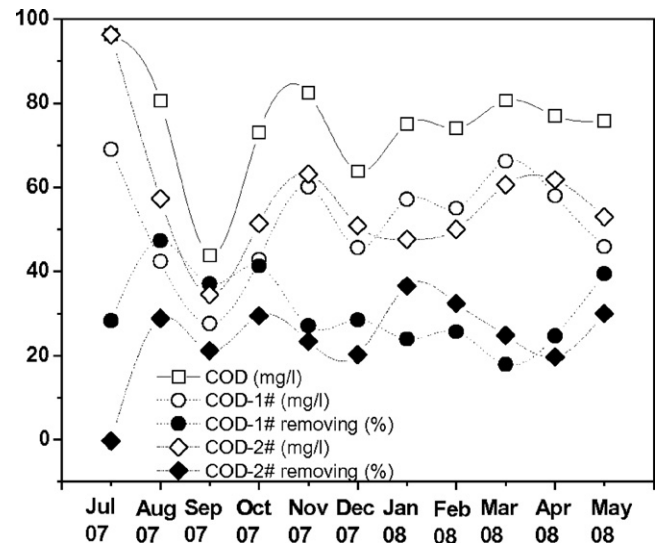


Fig. 5. COD removal from a vermifilter effluents through converter clog and coal cinder columns.

time going on, TP and DP removal rate of Column 2# was gradually higher than Column 1# due to higher amount of converter slag. But finally the difference was not evident. For nearly one year, the average removal rate of TP and DP by Column 1# were 44% and 56%, and by Column 2# were 42% and 54%, respectively. It can be known from the results that the mixture of converter slag and coal cinder as filter media was feasible for phosphorous removal from wastewater. Although higher amount of converter slag in Column 2#, it did not show significant superiority for P-removal. It can be attributed that the negative influence of organic matter on P sorption due to physical blockage of adsorption sites, or competition for sites by organic ions [42]. Simultaneously, microorganisms uptake, flushing or dilution via precipitation could cause a release of P that has been adsorbed by the converter slag [43].

The addition of coal cinder can also improve the effluent quality further [24–26], and the removal efficiencies of COD and $\text{NH}_4^+\text{-N}$ with time were investigated in Fig. 5. As illustrated in Fig. 5, both of the two columns were effective for COD removal. By an average

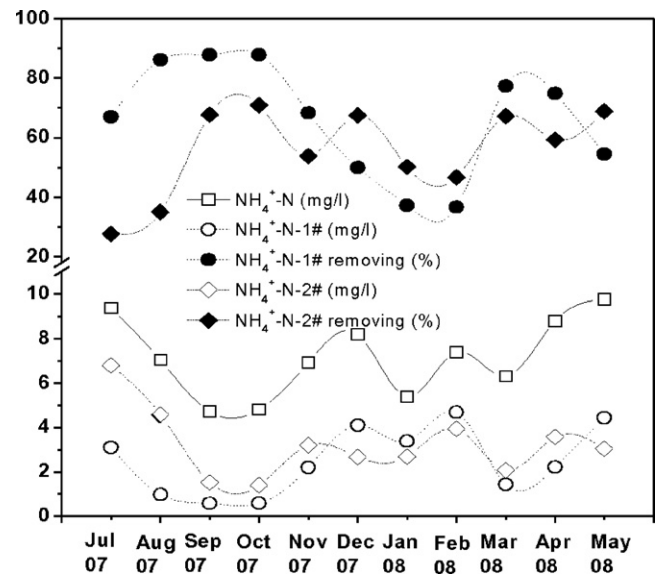


Fig. 6. Ammonia removal from a vermifilter effluents through converter clog and coal cinder columns.

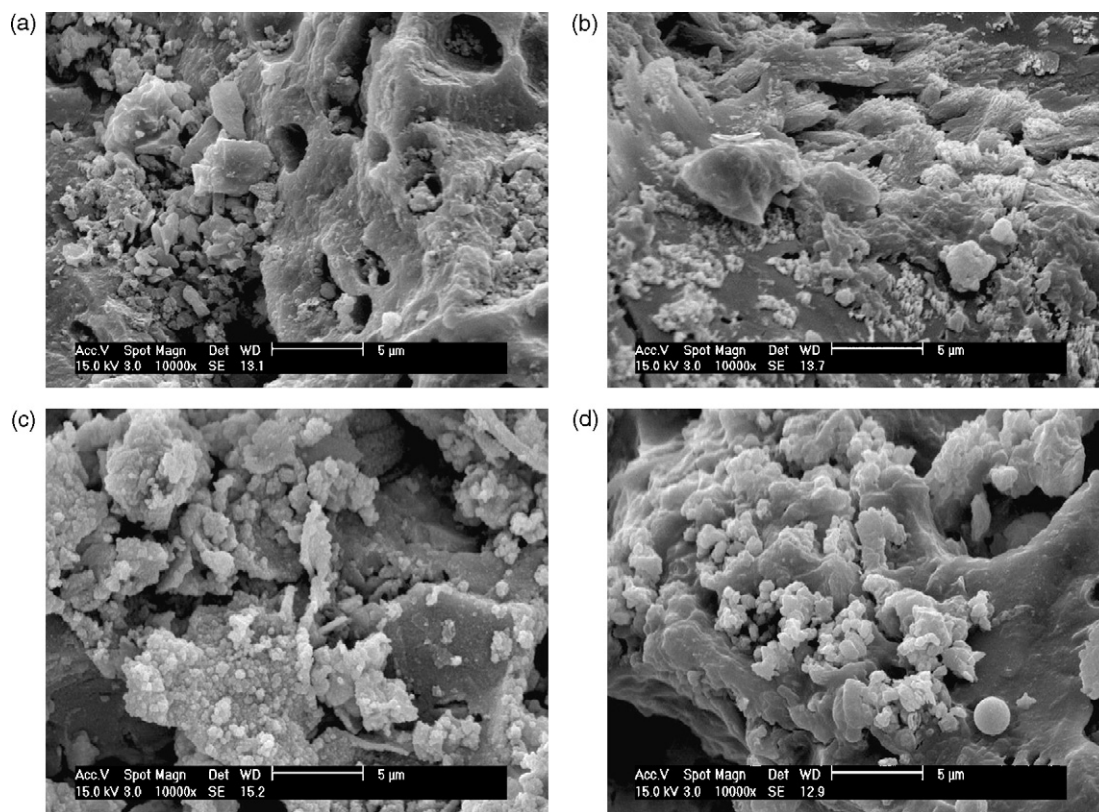


Fig. 7. SEM micrograph of the particles of coal cinder before (a) and after (b) phosphorous adsorption and converter slag before (c) and after (d) phosphate adsorption.

influent COD of 75.72 mg/L, the removal rate of Column 1# and Column 2# were 31% and 24%, respectively, and the effluent COD kept stable under 50 mg/L all the time. The effluent COD of Column 1# was lower than Column 2# due to more coal cinder for microorganism attachment and growth. The ammonia removal was very effective for the two columns (see in Fig. 6). In the beginning, the effluent ammonia was removed efficiently due to the large specific areas and strong ion sorption and exchange abilities of coal cinder in the two columns. The physical and chemical sorption played an important role for ammonia nitrogen removal at the beginning when the acclimations of microbes were not fulfilled. It is well known that biological nitrification is the most effective process for nitrogen removal [44]. Nitrification is generally carried out by aerobic, autotrophic bacteria that oxidize NH_4^+ to NO_2^- and NO_2^- to NO_3^- with molecular oxygen as an electron acceptor. Great specific surface area of coal cinder was benefit for organic matter remaining and microbial survival [23–25]. That, in turn, was benefit for biological nitrification. The biological nitrification was in highest flight for ammonia removal in the columns with time going on. In the same way, the significant difference of ammonia removal in two columns was still at the beginning, more coal cinders were advantaged for ammonia nitrogen removal. The average ammonia nitrogen removal rate for nearly one year by Column 1# was 67%, and by Column 2# was 57%. Column 1# was more effective for ammonia removal.

In order to study the particles surfaces before and after adsorption, scanning electron microscopic (SEM) images for the samples of raw adsorbents and adsorbents from column 1# were obtained at the terminative time of test. The micrographs were presented in Fig. 7. The micrograph of raw adsorbents showed the significant difference on the surface of converter slag and coal cinder. More micro-pores existed in the surface of coal cinder and abundant spherical metal oxides massed on the surface of converter slag, which can also explain why coal cinder had higher removal rate

for organic matter and ammonia, while converter slag had higher phosphorus removal ability. The micrograph (b) and (d) indicated that the pores of the adsorbents have been covered with adsorbate after a long-term operation, but the potential for longer operation was still existed due to the incompleteness occupied adsorption sites on the substrates surface.

4. Conclusions

The maximum adsorption capacity of converter slag and coal cinder was 2.417 and 0.398 mg P/g, respectively. The pH of solutions with converter slag and coal cinder would change dramatically and keep stable around pH of 8 in 8 h, and the influence of initial pH on phosphate removal by coal cinder was more significant than by converter slag. Based on the chemical composition of the converter slag and coal cinder and the appropriate solution pH, Fe content and Ca content contributed primarily to P immobilization in converter slag, and Al content contributed primarily to P immobilization in coal cinder. Phosphate removal rate by converter slag decreased with increase of initial phosphate concentrations. Results of two flow-through columns experiments indicated the feasibility of the mixture of converter slag and coal cinder as filter media for phosphorous removal from wastewater. And, the columns were also effective for the removal of organic matter and ammonia. The column with volume ratio of converter slag to coal cinder as 1:5 was better in the test due to the higher phosphorus removal efficiency and advanced wastewater treatment for a long time. Due to the low cost and high adsorptive capacity, the converter slag-coal cinder filters possess the potential to be utilized for cost-effective phosphorus removal and advanced wastewater treatment.

The investigations of anion and cation concentrations in the solution during the P-adsorption experiments should be explored further, which are important in study of the contributions mechanism for phosphorous removal by converter slag and coal cinder,

respectively. In addition, the long-term performance characteristics of converter slag and coal cinder columns need to be evaluated further before it can be recommended for critical application requiring guaranteed performance.

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References

- [1] U. Berg, D. Donnert, A. Ehbrecht, W. Bumiller, I. Kusche, P.G. Weidler, R. Nuesch, 'Active filtration' for the elimination and recovery of phosphorus from wastewater, *Colloid Surf. A: Physicochem. Eng.* 265 (2005) 141–148.
- [2] A.R. Jantrania, M.A. Gross, *Advanced Onsite Wastewater Systems Technologies*, CRC Press Inc., Boca Raton, Florida, 2006.
- [3] K. Sakadevan, H. Bavor, Phosphate adsorption characteristics of soils, slags and zeolites to be used as substrates in constructed wetland systems, *Water Res.* 22 (1998) 293–299.
- [4] A.S. Brooks, M.N. Rozenwald, L.D. Geohring, L.W. Lion, T.S. Steenhuis, Phosphorus removal by wollastonite: a constructed wetland substrate, *Ecol. Eng.* 15 (2000) 121–132.
- [5] L. Johansson, J.P. Gustafsson, Phosphate removal using blast furnace slags and opoka – mechanisms, *Water Res.* 34 (2000) 259–265.
- [6] Z. Brogowski, G. Renman, Characterisation of opoka as a basis for its use in wastewater treatment, *Pol. J. Environ. Stud.* 13 (2004) 15–20.
- [7] L. Johansson, Substrates for phosphorus removal potential benefits for on-site wastewater treatment, *Water Res.* 40 (2006) 23–36.
- [8] A.N. Shilton, I. Elmetri, A. Drizo, S. Pratt, R.G. Haverkamp, S.C. Bilby, Phosphorus removal by an 'active' slag filter—a decade of full scale experience, *Water Res.* 40 (2006) 113–118.
- [9] A. Drizo, Y. Comeau, C. Forget, R.P. Chapuis, Phosphorus saturation potential: a parameter for estimating the longevity of constructed wetland systems, *Environ. Sci. Technol.* 36 (2002) 4642–4648.
- [10] L. Johansson, Blast furnace slag as phosphorus sorbents column studies, *Sci. Total Environ.* 229 (1999) 89–97.
- [11] A. Drizo, C. Forget, R.P. Chapuis, Y. Comeau, Phosphorous removal by electric arc furnace steel slag and serpentinite, *Water Res.* 40 (2006) 1547–1554.
- [12] E.H. Kim, D.W. Lee, H.K. Hwang, S. Yim, Recovery of phosphate from wastewater using converter slag: kinetics analysis of a completely mixed phosphorous crystallization process, *Chemosphere* 63 (2006) 192–201.
- [13] S. Yim, E.H. Kim, A comparative study of seed crystals for the phosphorous crystallization process, *Environ. Technol.* 25 (2004) 741–750.
- [14] N. Ortiz, M.A.F. Pires, J.C. Bressiani, Use of steel converter slag as nickel adsorber to wastewater treatment, *Waste Manage.* 21 (2001) 631–635.
- [15] Y.X. Deng, H. Xu, Z.S. Zhong, L. Huang, Removal of phosphorus from waste water by steel slag, *Met. Mine.* 16 (2003) 49–51 (in Chinese).
- [16] L. Huang, Y.X. Deng, Experimental study on phosphorus adsorption and removal by BOF-slag, *Sichuan Environ.* 24 (2005) 5–8 (in Chinese).
- [17] Y.X. Deng, H. Xu, L. Huang, Application of steel slag in the process of phosphorus waste water treatment, *Non-ferrous Min. Metall.* 18 (2002) 43–45 (in Chinese).
- [18] J. Yang, Study on phosphorus removal effect in rapid infiltration column of steel slag and coal cinder mixture, Master Thesis, Tongji University, China, 2008.
- [19] L. Zeng, X.M. Li, J.D. Liu, Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings, *Water Res.* 38 (2004) 1318–1326.
- [20] J.P. Gustafsson, A. Renman, G. Reman, K. Poll, Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment, *Water Res.* 42 (2008) 189–197.
- [21] Deng Y.X., Study on removal of phosphorous in wastewater with natural minerals and steel slag, Ph.D. Thesis, China University of Geosciences, China, 2002.
- [22] E. Meers, D.P.L. Rousseau, E. Lesage, E. Demeersseman, F.M.G. Tack, Physical-chemical P removal from the liquid fraction of pig manure as an intermediary step in manure processing, *Water Air Soil Pollut.* 169 (2006) 317–330.
- [23] R.H. Zhang, F. Lei, Chemical treatment of animal manure for solid-liquid separation, *Transac. ASAE* 41 (1998) 1103–1108.
- [24] L.H. Cui, X.Z. Zhu, S.M. Luo, Y.H. Liu, Purification efficiency of vertical-flow wetland system constructed by cinder and turf substrate on municipal wastewater, *Chin. J. Appl. Ecol.* 14 (2003) 481–484 (in Chinese).
- [25] J. Zhang, X. Huang, C.X. Liu, Nitrogen removal enhanced by intermittent operation in a subsurface wastewater infiltration system, *Ecol. Eng.* 25 (2005) 419–428.
- [26] Q. Li, C.B. Kang, C.k. Zhang, Wastewater produced from an oilfield and continuous treatment with an oil-degrading bacterium, *Process Biochem.* 40 (2005) 873–877.
- [27] A. Drizo, C. Forget, R.P. Chapuis, Y. Comeau, How realistic are the linear Langmuir predictions of phosphate retention by adsorbing materials? 1st World Congress of the International Water Association, Paris, 2000 (Poster).
- [28] M.L. Aguilera, Purification of wastewater by vermifiltration, Ph.D. Thesis, University of Montpellier 2, France, 2003.
- [29] M.B. Bouché, J.P. Qiu, Concrete contributions of earthworms in the environmental study, *Doc. Pédzoool. Intégrol.* 3 (1998) 225–252.
- [30] M. Taylor, W.P. Clarke, P.E. Greenfield, The treatment of domestic wastewater using small-scale vermicompost filter beds, *Ecol. Eng.* 21 (2003) 197–203.
- [31] Y.S. Li, P. Robin, D. Cluzeau, M. Bouché, J.P. Qiu, A. Laplanche, M. Hassouna, P. Morand, C. Dappelo, J. Callarec, Vermifiltration as a stage in reuse of swine wastewater: monitoring methodology on an experimental farm, *Ecol. Eng.* 32 (2008) 301–309.
- [32] State Environmental Protection Administration of China, *Monitoring and Analysis Methods of Water and Wastewater*, fourth ed., China Environmental Science Press, Beijing, 2002 (in Chinese).
- [33] R.L. Parfitt, Anion adsorption by soils and soil materials, *Adv. Agron.* 30 (1978) 1–49.
- [34] N.J. Barrow, Modeling the effect of pH on phosphate sorption by soils, *J. Soil Sci.* 34 (1984) 751–758.
- [35] W.L. Lindsay, *Chemical equilibria in soils*, Wiley, New York, 1979.
- [36] S. Lasic, Microcrystalline hydroxyapatite formation from alkaline solutions, *J. Cryst. Growth* 147 (1995) 147–154.
- [37] W.A. House, The physico-chemical conditions for the precipitation of phosphate with calcium, *Environ. Technol.* 20 (1999) 727–733.
- [38] J.G. Chen, H.N. Kong, D.Y. Wu, X.C. Chen, D.L. Zhang, Z.H. Sun, Phosphate immobilization from aqueous solution by fly ashes in relation to their composition, *J. Hazard. Mater.* 39 (2007) 293–300.
- [39] J.B. Xiong, Z.L. He, Q. Mahmood, D. Liu, X.E. Yang, E. Islam, Phosphate removal from solution using steel slag through magnetic separation, *J. Hazard. Mater.* 152 (2008) 211–215.
- [40] B. Kostura, H. Kulveitová, J. Leško, Blast furnace slags as sorbents of phosphate from water solutions, *Water Res.* 39 (2005) 1795–1802.
- [41] N.M. Ageyi, C.A. Strydom, J.H. Potgieter, The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends, *Cem. Concr. Res.* 32 (2002) 1889–1897.
- [42] K. Sakadevan, H.J. Bavor, Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems, *Water Res.* 32 (1998) 391–399.
- [43] K. Syers, R.F. Harris, D.E. Armstrong, Phosphate chemistry in lake sediments, *J. Environ. Qual.* 2 (1973) 1–14.
- [44] C.M. Henze, P. Harremoës, Nitrification and denitrification in wastewater treatment, in: R. Mitchell (Ed.), *Water Pollution Microbiology*, vol.2, Wiley, New York, 1978, pp. 391–414.