



Phosphorus Removal from Wastewater by Steel Slag Ceramsite Filter

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ABSTRACT

Ceramsite made from steel slag was used as filter material in a packed column to remove phosphorus (P) from wastewater. Influences of both contact time and P concentration on reactor performance were investigated. Additionally, chemical and mineralogical analyses were conducted to determine the mechanism of phosphorus removal. Results showed that Ca²⁺ and OH⁻ were released from ceramsite to remove phosphorus from liquid phase under alkaline condition. Nevertheless, suitable retention time facilitated the efficient use of Ca²⁺ for phosphorus removal. Under the optimal contact time (4h), P removal capacity of ceramsite media was 7.9 mg/g for 140 days (at influent concentration of 10 mg/L), and the impact of influent concentration (0.5~10 mg/L) on P removal was neglectable. The mechanism for P removal included solid dissolution, precipitation and surface adsorption, among which the dissolution of calcium and Ca-P precipitation were overwhelming. The Ca-P products proved to be poorly crystalline tricalcium phosphate (TCP) and carbonated apatite.

INTRODUCTION

Phosphorus in surface water may promote the eutrophication problem (Liu et al. 2009). And phosphorus removal from wastewater was considered as the most important way to control phosphorus pollution. Nowadays, the standard of P discharge has become more and more stringent, which encourages researchers to seek economic and efficient material for P removal. Worldwide, low-cost materials for P removal became attractive in the last two decades (Khadhraoui et al. 2002, Yang et al. 2012). Several studies demonstrated that steel slag has a high affinity for P binding (Pratt et al. 2009, Barca et al. 2014, Yun et al. 2015, Li et al. 2018). However, the irregular shape of steel slag causes the risks of compaction and cogging for long-term operation. Besides, its adsorption capacity for phosphorus is limited in surface area due to lower porosity.

Previous studies showed that porous ceramsite made from steel slag exhibited excellent feature in phosphorus removal (Liu et al. 2016). However, P-removal performance of ceramsite in continuous flow reactor needed further investigation, especially for the long-term running, and the mechanism of phosphorus removal remained uncertain. In this study, steel slag ceramsite was employed as the packing material of filter to remove phosphorus from synthetic wastewater. The influences of influent P concentration and contact time on P removal were studied, and dissolution of

Ca²⁺ and OH⁻ from ceramsite was analysed. In addition, chemical and mineralogical analyses were employed to investigate the mechanisms of P removal by steel slag ceramsite.

MATERIALS AND METHODS

Preparation of ceramsite: The steel slag was BOF (basic oxygen furnace) slag from a local steelworks. After crushed and sieved through 200 mesh, the slag powder was dried at 105°C. The dry slag powder was mixed with clay and flour in ratio of 5:2:1 (W/W), and then granulated to 3~5 mm particles in a disc pelletizer with tap water (40% of total weight) added in. The particles were air dried at room temperature for 48h and sintered in a muffle furnace at 1000°C for 30 minutes.

Construction and operation of steel slag ceramsite filter: As shown in Fig. 1, the packed column was 50 cm in height, with inner diameter of 7 cm. The height of filter part was 35 cm and the supporting layer was 5 cm. The apparent density of supporting part and filter part was 1.65 g/cm³ and 1.37 g/cm³, respectively with the porosity of 43% and 53%. Synthetic wastewater, which was prepared by KH₂PO₄ and water, was introduced from filter bottom. The flow rate was set in the range of 1.4 m/d~4.5 m/d, leading to different contact times.

Continuous flow experiments of filter:

Phosphorus removal from wastewater under different

contact times: Three filters were operated with different contact times, i.e. 1.5 h, 4 h and 6 h, and the influent P concentration was maintained at 10 mg/L.

Phosphorus removal from wastewater under different influent P concentrations: A filter was operated with changed P concentration (10 mg/L→0.5 mg/L) under the optimal contact time (4 h).

Ca²⁺ dissolution from steel slag ceramsite: Tap water was substituted for wastewater to flow through the filter with a contact time of 4 h. During the operation, PO₄³⁻-P, Ca²⁺ and pH were monitored.

Chemical extraction of P: Ceramsite samples were first air dried at 30°C to constant weight. The samples were then crushed to powder, and performed sequential chemical extraction according to Headley (Headley et al. 2003). First, 2g of the sample was extracted for P in 100 mL NaHCO₃ solution (0.5 M) for 16 h; the extraction represented weakly bound phosphorus (W-P), which was combined through adsorption. Second, the residue extracted by NaHCO₃ was extracted in a 100 mL NaOH solution (0.1 M) for 16 h; the extraction represented Fe and Al associated P (Fe/Al-P). Then the residue extracted by NaOH was leached at room temperature for 16 h with 100 mL HCl (1 M) with continuous agitation; the extraction substitutes for Ca associated P (Ca/Mg-P), which was combined through chemical reaction and adsorption. Finally, the residue was extracted in 40 mL HCl (12 M) at 80°C water bath for 20 min. This fraction represented P in very stable compounds (S-P). After each step, samples were successively washed with 25 mL KCl (1 M) and 25 mL water. Fresh ceramsite was as a blank sample and

deducted from the corresponding extracted P fraction.

Characterization analysis for filter material: Surface morphology and elementary composition of both ceramsite (fresh and used) and crystal from the filter was analysed by SEM-EDX (SEM: Hitachi S-4800, EDX: Thermo Fisher Noran7). Surface samples stripped from the used ceramsites were performed mineralogy analysis through X-ray diffraction (XRD, D/MaX2500PC, at 40 kV and 100 mA, Cu/kα) and Fourier transform infrared spectroscopy (FTIR, Shimadzu IR Affinity-1s, KBr squash method).

PO₄³⁻-P was analysed by molybdate spectrophotometric method (Chinese SEPA 2002). Ca was determined through titration method. All chemicals used were of analytical grade.

RESULTS AND DISCUSSION

Phosphorus removal: Fig. 2 exhibited the P-removal effect of slag ceramsite filter under different condition. Result showed that over 90% of phosphorus was removed by the ceramsite filters during the high-efficiency stage. Better P removal effect (meaning stable and long-term operating) was observed as contact time was set at 4 h and 6 h compared to 1.5 h (Fig. 2a), which indicated that sufficient contact time was needed for P-removal by ceramsite filter. Total phosphorus removal amount to 4.6 mg/g, 7.9 mg/g and 5.3 mg/g for 1.5 h, 4 h and 6 h respectively. 4 h was proved to be the optimal contact time for stable and maximized P-removal. Since Ca²⁺ was consumed by carbonate and phosphate simultaneously, Ca-P precipitation was influenced by the available amount of Ca²⁺ for phosphate. Shorter intention incurred too much Ca²⁺ flowing away from the sys-

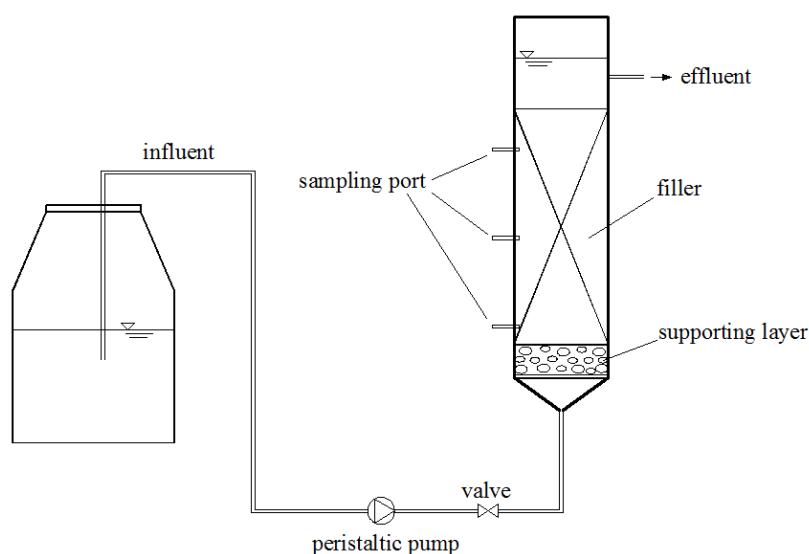


Fig. 1: Schematic of the experimental setup.

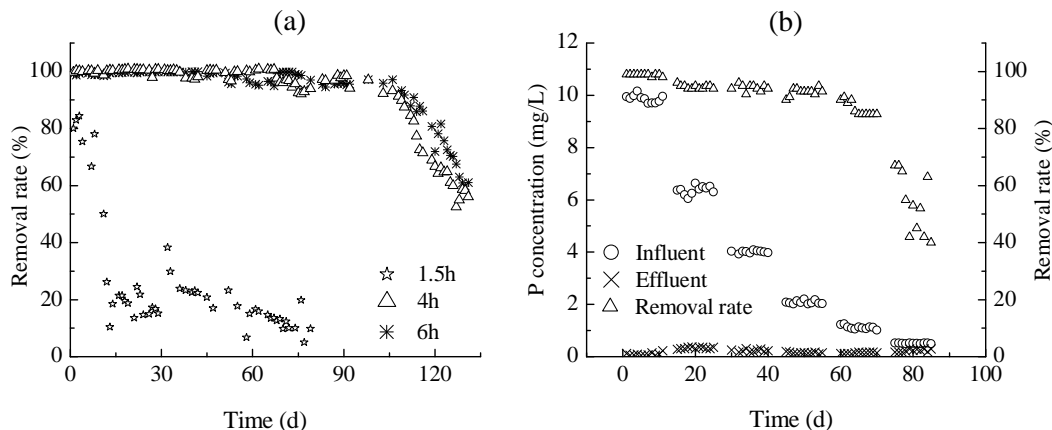


Fig. 2: Influences of contact time (a) and influent P concentration (b) on P removal.

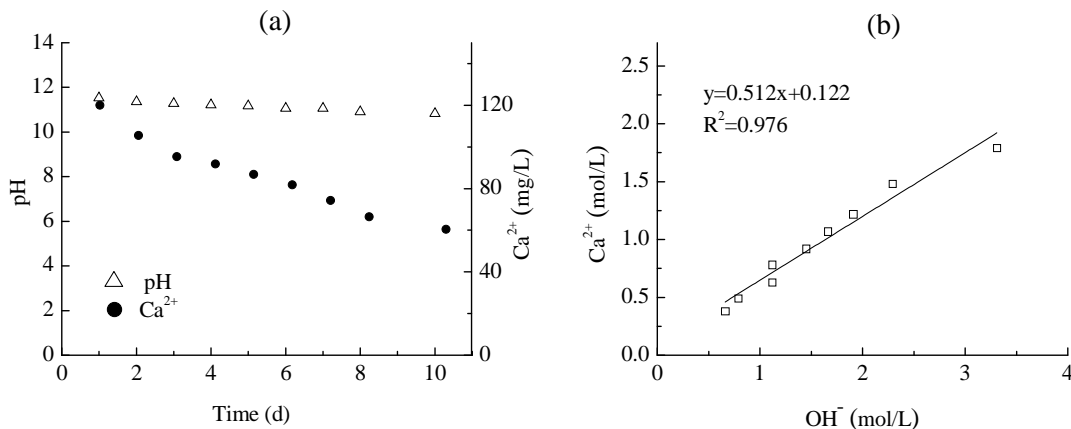


Fig. 3: Ca²⁺ and pH in the effluent from the filter with tap water as influent (a) and their relationship (b).

tem, whereas longer detainment might encourage the competition of CO₃²⁻ for Ca²⁺ with phosphorus (Liira et al. 2009, Navarro et al. 2010, Blanco et al. 2016). Under the optimal contact time, effluent P concentration of the ceramsite filter maintained in 0.1 mg/L~0.3 mg/L, as influent phosphorus ranged in 0.5 mg/L~10 mg/L (Fig. 2b), suggested a good adaptability of the filter for low strength phosphate. In the case of secondary-effluent upgrading in WWTP, further reduction of phosphorus is a typical problem, thus slag ceramsite filter may have a broad possibility in this field.

Effluent Ca²⁺ and pH: Alkali and Ca-rich slag have been proved to remove phosphorus through precipitation by releasing Ca²⁺ and OH⁻ into liquid phase. This feature was related to the presence of CaO or Ca(OH)₂ (Barca et al. 2013, Okano et al. 2013, Barca et al. 2014). Fig. 3 showed that effluent Ca²⁺ and pH gradually decreased with the operat-

ing time, and the strength of effluent Ca²⁺ was in proportion to OH⁻ [OH⁻ was calculated according to equation (1)]. The fitting relation between Ca²⁺ and OH⁻ was in accordance with equation (2), which indicated the existence of Ca(OH)₂ in liquid phase. Considering that the slag ceramsite was roasted before utilizing, Ca(OH)₂ might be derived from the reaction between CaO and water.

$$[OH^-] = \frac{10^{-14}}{10^{-pH}} \quad \dots(1)$$



It was beneficial for P precipitation with free Ca²⁺ that Ca²⁺ release accompanied by pH increase. In Fig. 4, higher effluent Ca²⁺ and higher pH occurred concomitantly with lower effluent P (despite the change of contact time), which could be attributed to the facilitated reaction between Ca and P. Under the retention time of 4 h or 6 h, higher pH (>10

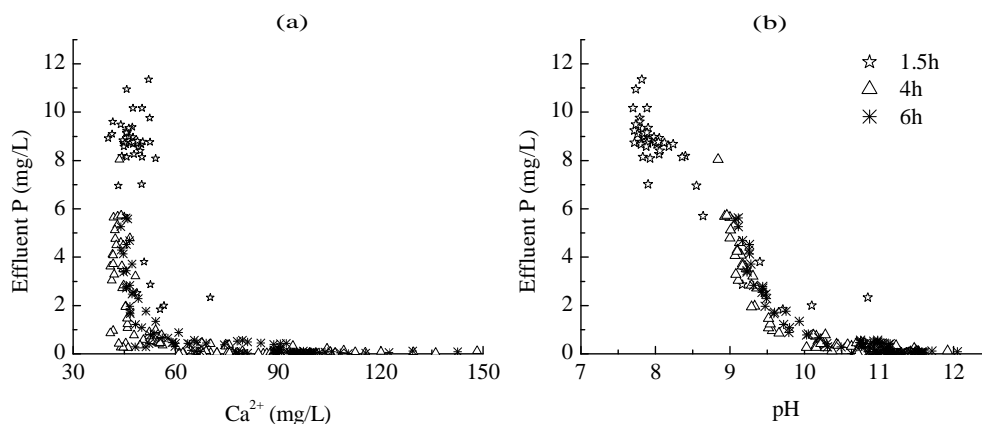


Fig. 4: Relationships between Ca²⁺ (a), pH (b) and effluent P.

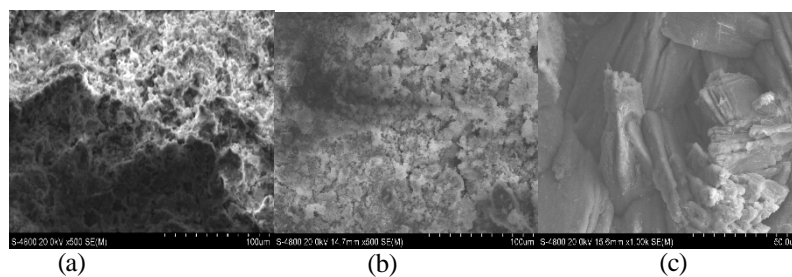


Fig. 5: SEM images of ceramsite and filter crystal. a. Fresh ceramsite b. Used ceramsite (40d) c. Crystal

Table 1: Elementary content of the SEM samples (%W).

Samples	C	O	Mg	Al	Si	P	Cl	Ca	Fe
Fresh ceramsite	4.33	47.27	1.46	5.96	12.54	-	-	17.75	10.68
Used ceramsite (40d)	7.46	49.56	7.67	0.81	10.02	3.05	-	21.42	-
Crystal	7.82	43.71	2.30	-	2.04	2.87	2.87	38.37	-

Note: "-" not detected.

in Fig. 3a) and sufficient Ca²⁺ (more than 60~70 mg/L in Fig. 3b) brought a P concentration less than 0.5 mg/L, which corresponded to the first two months of the filters. During the operation, influent Ca²⁺ was 40~45 mg/L, and pH ranged in 7.5~8.0. As effluent Ca²⁺ concentration decreased below 50 mg/L (close to the raw level) and effluent pH was below 9.5, P removal was dramatically deteriorated. Thus, the critical Ca²⁺ concentration and pH of the effluent for a stable and effective performance could be concluded. It is notable that a serious depletion of effluent Ca²⁺ was found compared to pH decline, namely that effluent Ca²⁺ diminished from 140~150 mg/L to 50~60 mg/L in about three months, while pH remained above 10 until day 103 for 4 h filter (and day 112 for 6 h filter). Considering that CO₃²⁻

was dominant at higher pH, the lagging descent of pH may relate to the buffering of carbonate.

Morphology and mineralogy analysis of the product:

SEM observation revealed that the fresh ceramsite had a porous surface, which was covered by massive precipitates after 40 days of operating (Fig. 5). In contrast with the irregular sediment grown on the surface of filter material, the crystals formed in the filter bed seemed compact and regular. Table 1 displayed the EDS results corresponding to Fig. 5. C, Mg, P and Ca were found concentrated in the ceramsite surface after filtration, confirming that P combination was relevant to these elements. It seemed that the crystal sediment was certain type of calcium salt, since Ca content was much higher in it.

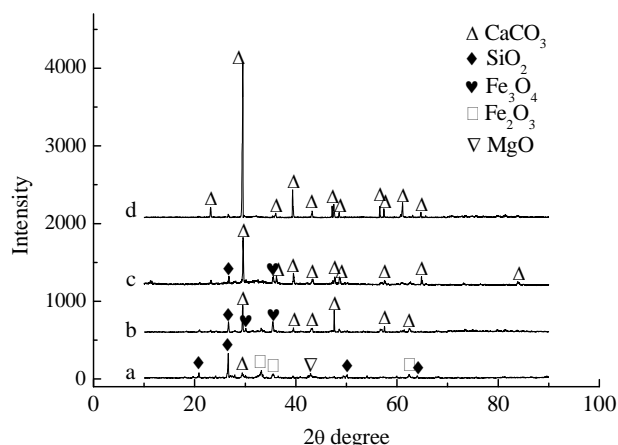


Fig. 6: XRD analysis of ceramsite and crystal. a. fresh ceramsite b. used ceramsite(40 d) c. used ceramsite (140d) d. crystal

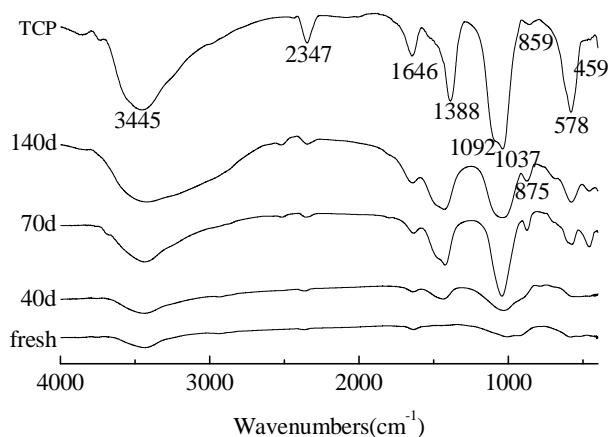


Fig. 7: FTIR spectrum of ceramsite at different filter stages.

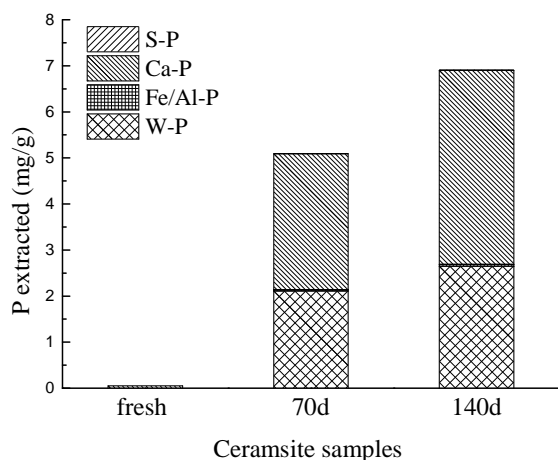


Fig. 8: P-extraction from ceramsite filter at different stages.

XRD analysis (Fig. 6) showed that the intensity of CaCO_3 in the used ceramsite (40 d and 140 d) increased significantly compared to the fresh one, and a contrary trend appeared in SiO_2 phase. CaCO_3 was found dominant in the crystalline phase. No crystalline phase of phosphate was detected, that may relate to their poor crystallinity in the experiment.

As shown in Fig. 7, the absorption of 3445 cm^{-1} and 1646 cm^{-1} (corresponding to ν_1 and ν_2 modes of the O-H) attributed to the absorbed water. The peaks at 1388 cm^{-1} and 875 cm^{-1} belong to CO_3^{2-} (ν_3 and ν_2 modes). Additionally, the peaks at 1092 cm^{-1} (weak), 1037 cm^{-1} , 578 cm^{-1} and 459 cm^{-1} attributed to PO_4^{3-} (ν_3 and ν_4 modes). The absorption of CO_3^{2-} and PO_4^{3-} increased with the operating time (140 d > 70 d > 40 d > fresh ceramsite), suggesting an increasing content. The phosphate peak of used ceramsite was in accordance with TCP, and peaks of CO_3^{2-} and PO_4^{3-} emerged simultaneously, that conformed to the infrared characteristics of carbonated apatite (Rau et al. 2010). Considering that no crystalline phase was detected by XRD detection, it was likely that phosphorus participated in the precipitation of CaCO_3 or CO_3^{2-} attended in the reaction of Ca-P. Therefore, TCP and carbonated apatite were suggested as the products of P removal by ceramsite.

Chemical extraction of P: Previous study showed that phosphorus removal was related to Ca-P precipitation. However, other combination forms of phosphorus might exist. Thus, chemical extractions for phosphorus were carried out. Fig. 8 revealed that the P removal products of the filter material were mainly W-P and Ca-P, which summed to over 98% of the total. The amount of Fe/Al-P and S-P were negligible. Comparing the samples from day 70th and day 140th, TP increased from 5.09 mg/g to 6.91 mg/g, which resulted mainly from the gain of Ca-P fraction. It can be confirmed that phosphorus was in bondage to slag ceramsite by surface adsorption together with Ca-P precipitation. And surface adsorption tended to saturation gradually during the later operation stage.

Ca-P precipitation was typically considered as the most important way for phosphorus removal by steel slag from BOF (Pratt et al. 2009, Barca et al. 2013, Barca et al. 2014, Blanco et al. 2016). The existing form of PO_4^{3-} in solution was affected by pH environment, which influenced the binding mode of calcium and phosphorus. HPO_4^{2-} is the dominant phosphoric ion species in the pH range of 7.5-10.0 (Okano et al. 2013), which react with Ca^{2+} to form products including dicalcium phosphate (DCPD), octacalcium phosphate (OCP), tricalcium phosphate (TCP), and apatite (Barca et al. 2013). DPCD and OCP were confirmed as the precursor or metastable product at moderate to low pH, while TCP

and apatite tend to dominate at higher pH. During the operation, better P removal was in accordance with higher effluent pH above 10, at which alkaline TCP and apatite may be predominant. However, no crystallization of TCP or apatite was detected in the ceramsite media. This may be attributed to the participation of carbonate. The slow filtering velocity resulted in carbonate saturation in the liquid phase. CO_3^{2-} competed for Ca^{2+} with phosphate, and took part in Ca-P precipitation to debase the product crystallinity.

It was interesting that the percentage of weakly bound P in ceramsite filler amount for as much as 40% of the total, which was much different from Ca-rich steel slag (little W-P was detected in the steel slag filler from EAF or BOF (Barca et al. 2014)). It was likely that the porous structure of slag ceramsite provided larger specific surface area and more reactive site for phosphorus adsorption. The surface hydroxylation of certain amorphous oxides such as OH⁻ in Ca-OH linkages, were considered favourable for P adsorption through ion exchange (Okano et al. 2013).

Phosphorus removal mechanism by steel slag ceramsite:

The P removal mechanisms by steel slag ceramsite from above findings can be described as follows:

1. **Adsorption:** Loose adsorption onto the porous surface of steel slag ceramsite and chemical adsorption onto oxide/hydroxide. The percentage of this part amounted to about 40% in total, which tended to saturation in the long run.
2. **Precipitation:** Poorly crystallized TCP and carbonated apatite, or amorphous Ca phosphate precipitated concomitantly with CaCO_3 on the surface of slag media. The form of these compounds was related to the operational conditions. The experimental conditions such as low inlet content, small filtering velocity, and the short-term filter operation, led to low supersaturation and carbonation, which were unsuitable for product crystallization since the development of crystal phase needed a certain supersaturation or longer period (Barca et al. 2013).

CONCLUSIONS

1. Steel slag ceramsite was an excellent filter material for phosphorus removal. Filter column experiment showed that the optimal contact time was 4 h for 10 mg-P/L influx. Under this contact time, efficient and stable phosphorus removal was observed despite influent phosphorus changed (from 1 mg/L to 10 mg/L). It was found that the higher Ca^{2+} concentration and pH values occurred in effluent, the better phosphorus removal was.
2. The mechanism of phosphorus removal by steel slag ceramsite including solid dissolution, Ca-P precipita-

tion and surface adsorption. Ca-P precipitation was flourished by Ca^{2+} and OH⁻ released from alkali component.

3. Poorly crystallized TCP and carbonated apatite were inferred in the precipitation.

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