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Full Length Research Paper

Phosphorus removal from wastewater by fly ash ceramsite in constructed wetland

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Fly ash ceramsite-assisted phosphorus (P) removal from wastewater was investigated in this paper. First, the basic physical and chemical properties of two types of fly ash ceramsites were outlined. The adsorption capacity of P in wastewater was then examined by static interval experiments, in which the influence of temperature and contact time was investigated. The maximum adsorption capacity of the fly ash ceramsite of P was 0.892 mg g^{-1}, and their adsorption processes were described by a single - level variable dynamic model, in which the correlation coefficients were > 0.85. Furthermore, the fly ash ceramsite with higher P adsorption capacity was applied in a constructed wetland as a substrate to continuously treat wastewater. It is noteworthy that the adoption of fly ash ceramsite in such an environment significantly improved P removal from wastewater: the total P and dissolved orthophosphate in the effluent after treatment were < 0.40 mgL^{-1} and < 0.20 mgL^{-1} respectively and the P-removal rate reached 90%. The results indicate that fly ash ceramsite can be used as a high - efficiency substrate in constructed wetlands to enhance P removal, and can reduce the area required for constructed wetlands.

Key words: Fly ash ceramsite, constructed wetland, ceramic substrate, phosphorus removal.

INTRODUCTION

A constructed wetland is a complex ecosystem that combines physical (example, filtration and adsorption), chemical (example, ion exchange and precipitation) and biological (example, microbial decomposition and plant assimilation) treatment mechanisms together, and is therefore an ideal platform for removing organic matter, nitrogen and phosphorus (P) from wastewater (Ham et al., 2010). The removal efficiency for biochemical oxygen demand and suspended solids by constructed wetlands is quite high, but for P it is lower (only 30% in conventional processes) (Song and Zhao, 2006). Thus, increasing the P removal efficiency in constructed wetlands has become a focus of current research. For a constructed wetland, the P removal is mainly done by the substrate and so it is important to choose an appropriate substrate with good P - adsorption ability (Brix et al. 2001; Yuan and Jing, 2005). Fly ash ceramsite made, from fly ash, a solid waste of power plants, shows promise as an ideal substrate; it has a rough surface, a porous structure and a low price. More importantly, it not only possesses active sites such as aluminum, silicon oxide that have good adsorption performance of pollutants in wastewater, but also contains some calcium (Ca), iron (Fe) and other components that can react with pollutants. Thus, it has been widely used as a substrate in the treatment of municipal sewage and industrial wastewater (Xiang and Li, 2006).

In the present study, two types of fly ash ceramsite made from different fly ashes were used. Their physical structures, chemical composition and adsorption ability for P were systematically examined. Furthermore, the fly ash ceramsite with higher P adsorption capacity was applied in a constructed wetland as substrate to continuously treat wastewater containing P. The P - removal characteristics of such fly ash ceramsite were then investigated in detail. The results contribute toward the maintenance and management of constructed wetlands using fly ash ceramsite as a substrate.

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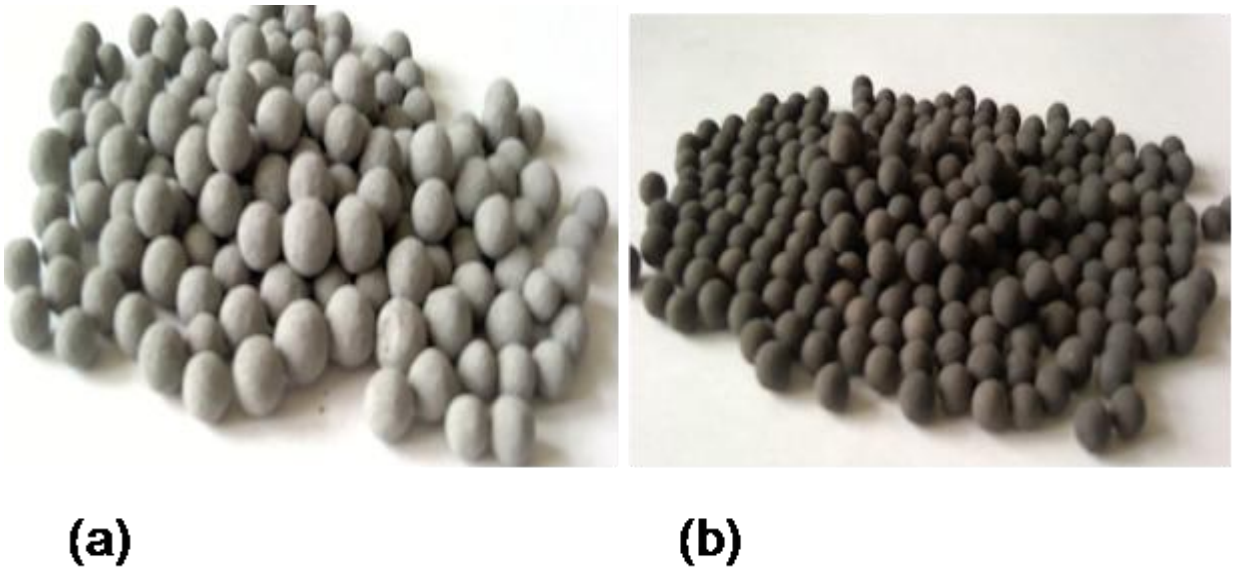

Figure 1. Optical images of two types of fly ash ceramsites: (a) Number I and (b) Number II.

Table 1. Fly ash ceramsite chemical elements (weight %).

Fly ash ceramsite	O	Mg	Al	Si	K	Ca	Ti	Fe	Cl	Na	C
Number I	49.3	4.05	6.17	18.73	0.77	2.36	0.38	3.28	1.49	0.71	12.76
Number II	54.09	0.47	7.5	14.41	0.58	20.56	0.31	2.07	0	0	0

MATERIALS AND METHODS

Sources of material and physical and chemical properties

The raw materials of fly ash ceramsite selected were made from two different power plants (Figure 1); Numbers I and II spherical fly ash ceramsite which had a slight color difference in appearance. To ensure that the substrates had the greatest possible surface area and sufficient porosity to avoid congestion at the same time, the fired ceramic particle sizes used were 3 to 5 mm (Zhu and Zhu, 2000). The chemical elements of the two kinds of fly ash ceramsites were tested by spectrometry (Table 1). The elements contained in the two types of fly ash ceramsites were mainly oxygen, silicon, aluminum, Fe and Ca, but the weight and atomic compositions varied greatly. The weight of Ca in fly ash ceramsite Number I was 23.16% and the atomic composition was 12.13%. That is, it is a high-Ca fly ash. Fly ash ceramsite Number II had 8.67% carbon, since it was not completely oxidized during the firing process.

The surface structure and internal pore structure of fly ash ceramsite Numbers I and II were determined by electron microscopy (Figure 2), which showed that Numbers I and II fly ash ceramsite's surface and internal pores were both more developed than traditionally constructed wetlands substrate such as soil or gravel. However, fly ash ceramsite Number I had an internal crystal structure, which is conducive to physical and chemical adsorption and forming biofilms.

The internal porosity of fly ash ceramsite Numbers I and II were determined using a pressure mercury analyzer. The average pore sizes of the two fly ash ceramsites were slightly different at 20.4 and 22.0 nm, respectively. However, the porosity of fly ash ceramsite Number II which was 54.69% with a pore area of 79.605 $m^2\ g^{-1}$ was higher than that of Number I with porosity of 47.83% and pore area of 23.325 $m^2\ g^{-1}$. The basic theory of physical adsorption indicates that the adsorption capacity of fly ash ceramsite Number II should be higher than that of Number I.

Static experiment on fly ash ceramsite adsorption of soluble orthophosphate (PO_4^{3-}) in water

The adsorption of solid adsorbent solute in solution can be described by a single-level dynamic model [7], The differential form is:

$$\frac{d_c}{d_t} = -k_1 c$$

The common expression is:

$$q_t = A(1-e^{-k_1 t})$$

In the expression: qt is the P adsorption capacity by fly ash ceramsite ($mg \cdot kg^{-1}$); t is contact time (h); k_1 is the single-level kinetic rate constant (h^{-1}); A is the related coefficient with initial concentration;

To determine the best adsorption capacity load, different weights of the two fly ash ceramsites were placed into 100 ml of 5 mg L^{-1} of PO_4^{3-} solution, respectively, and oscillated fully (speed 160 revolutions min^{-1}) at specific temperatures. The preliminary experiment showed that 20 g of fly ash ceramsite had the maximum adsorption capacity, and so this amount was used to study adsorption. Every hour, 5 ml of supernatant was removed and filtered through filter paper and tested until the P concentration no

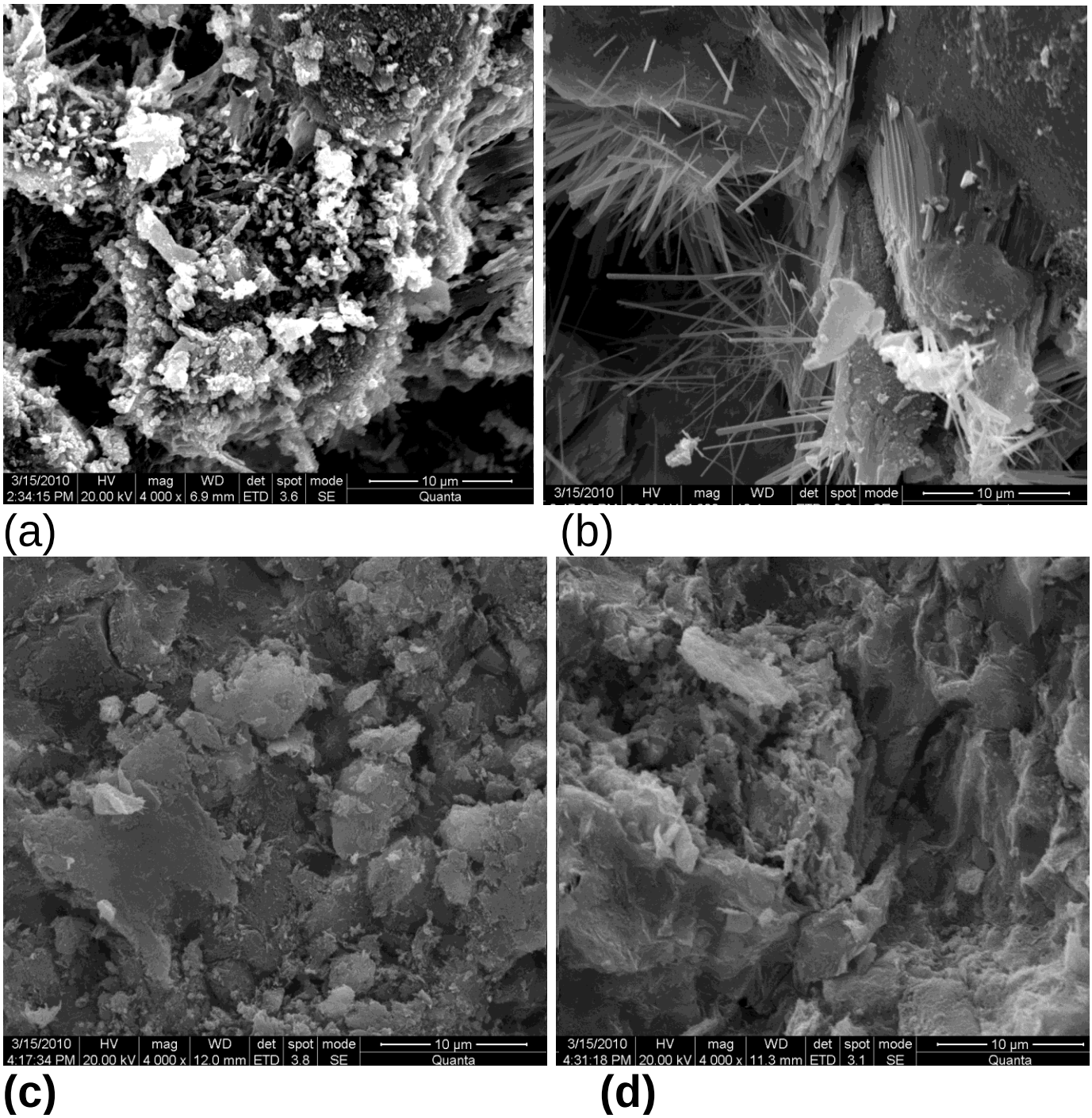

Figure 2. SEM images showing the surface [(a) and (c)] and the cross-section [(b) and (d)] morphology of fly ash ceramsite Numbers I and II.

longer changed. The P adsorption capacity and adsorption rate of fly ash ceramsite were determined from the PO_4^{3-} concentration change. The shaker temperature was set at 15 ± 1.20 ± 1 or 25 ± 1°C, respectively, to determine the effect of temperature on PO_4^{3-} adsorption capacity. The PO_4^{3-} concentration was determined by Anti-Mo-Sb spectrophotometry (8). (Standard Method for the Examination of Water and Wastewater. Editorial Board, Beijing, 2002).

Continuous experiment on fly ash ceramsite-assisted P removal in a constructed wetland environment

The NO.II fly ash ceramsite with higher adsorption capacity, as determined from the basic physical and chemical properties and P adsorption experiments, was added into a constructed wetland of conventional substrate design [9] Li and Zeng (2009) (Figure 3) with

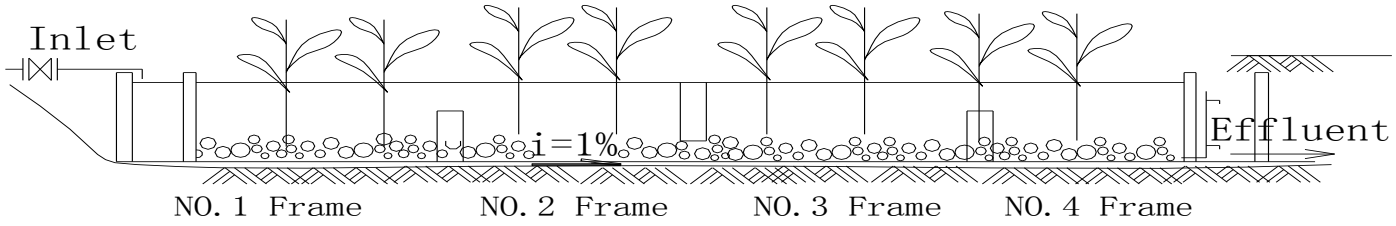

Figure 3. Profile of the constructed wetland.

four frames of 1.5 m width and 6.4 m length and which could treat 5 m^3 d^{-1} of effluent. The effluent was contaminated river water which had been pretreated by a biological filter. A 500 mm wide distribution channel was set in front, and a 1 × 1.5 m clearing pool at the end of the constructed wetland. Gravel (30 cm deep) was settled at the bottom of the constructed wetland and fly ash ceramsite was used as the middle layer to enhance P removal, and then a 25 cm layer of sand was placed on top to maintain plant roots. The continuous experiment was performed outdoors in summer to enable sufficient sunlight for aquatic plants. *Cyperus alternifolius* (cyperaceae summer-green sedges genera) which has a large root system was planted in the first three frames and *Canna indica* (Canna families, canna genera) were planted in the fourth frame. The environmental temperature was 25 to 30°C.

The continuous experiment had two stages. In the first stage, the system was continuously run until the P-removal rate from wastewater was stable. The P-removal characteristics using fly ash ceramsite was investigated at this stage. The second stage began when the removal rate was stable, and three sampling ports located in the three respective frames along the wetland were then used to study the change in P-removal along the wetland. Because the water which was treated was actually contaminated river water, the P in water had different forms. To comprehensively study the fly ash ceramsite's P-removal capability, both the total P (TP) and soluble reactive phosphate salt (PO_4^{3-}) were tested. The PO_4^{3-} concentration was tested by the Anti-Mo-Sb spectrophotometry; TP concentration was determined by the same method following water sample digestion with per sulfate [8] (Standard Method for the Examination of Water and Wastewater, Editorial Board, Beijing, 2002). The ranges of TP and PO_4^{3-} in effluent water were 1 to 1.8 and 0.8 to 1.4 mg L^{-1}, respectively.

RESULTS AND DISCUSSION

Static experiment on PO_4^{3-} adsorption by fly ash ceramsite

The PO_4^{3-} adsorption kinetics characteristics of fly ash ceramsite Numbers I and II were determined at different temperatures (Figure 4). The PO_4^{3-} adsorption was consistent with the Langmuir isotherm equation - as temperature increased, adsorption capacity became greater. Temperature is a major factor influencing adsorption. As temperature increases, the energy of PO_4^{3-} overcomes the resistance of the fly ash ceramsite surface-film and allows P proliferation in the internal pores of the fly ash ceramsite, and so the availability of surface adsorption sites increases [10] (Zhao and Zhou, 2007). Fly ash ceramsite Number I was more affected by temperature than Number II, but the adsorption capacity increased a little when the temperature increased from 20 to 25°C, implying that when the temperature reached a certain point, the adsorption capacity no longer increased.

The PO_4^{3-} adsorption capacity of the two types of fly ash ceramsites was very different. Fly ash ceramsite Number I adsorbed 93.7% of P in the water at 25°C and the adsorption load was 0.892 mg g^{-1}. However, Number II only adsorbed 64% of P in the water at 25°C and the adsorption load was only 0.590 mg g^{-1}. The adsorption of P in water by fly ash ceramsite had two facets. On one hand, the P in water diffused to the surface of fly ash ceramsite, which had a huge surface area and surface activity of adsorption sites for P adsorption. On the other hand, P reacted with the Ca of the fly ash ceramsite and was then deposited on the fly ash ceramsite surface [10] (Zhao and Zhou, 2007). Fly ash ceramsite Number I was made from high-Ca fly ash, and so could adsorb more P than did Number II. The Ca content of fly ash ceramsite Number I was 10 times that of Number II, so theoretically, the P adsorption capacity of the former should be 10 times that of the latter. However, the actual result was only 1.5 times. This indicated that P adsorption capacity was not only related to the Ca content of the fly ash ceramsite, but that the surface adsorption energy of the fly ash ceramsite played an important role during the adsorption process.

The P adsorption capacity of the two types of fly ash ceramsite increased as the contact time increased (Figure 5). When the contact time was 3 h, the adsorption capacity of fly ash ceramsite Number I was 1.28, 1.06 and 1.03 times that of the corresponding values when the contact time was 1 h for 15, 20 and 25°C, respectively. For fly ash ceramsite Number II, the respective rates were 1.03, 1.05 and 1.04 times. The contact time affected phosphate adsorption capacity, particularly for fly ash ceramsite Number I. When contact time increased, the physical adsorption and chemical deposition also increased, and the P adsorption capacity was larger homogenously. For 15, 20 and 25°C, the adsorption equilibrium got all within 3 h, which implied that the temperature of adsorption equilibrium gain time effect was small. The P adsorption process was accurately described by a single-level one - level dynamic model (Table 2) with correlation coefficients around 0.90 q_{max}

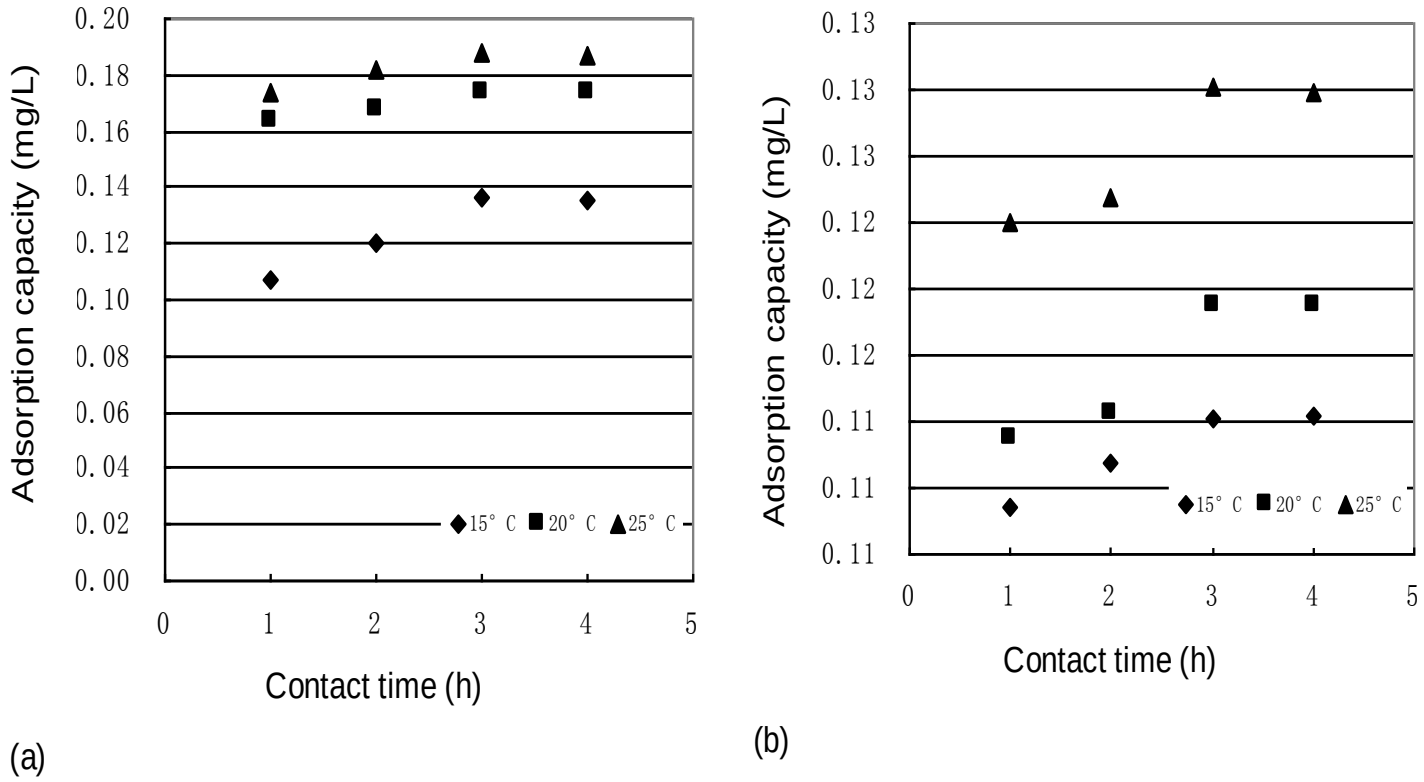

Figure 4. The P adsorption performances of (a) fly ash ceramsite Number I and (b) fly ash ceramsite Number II.

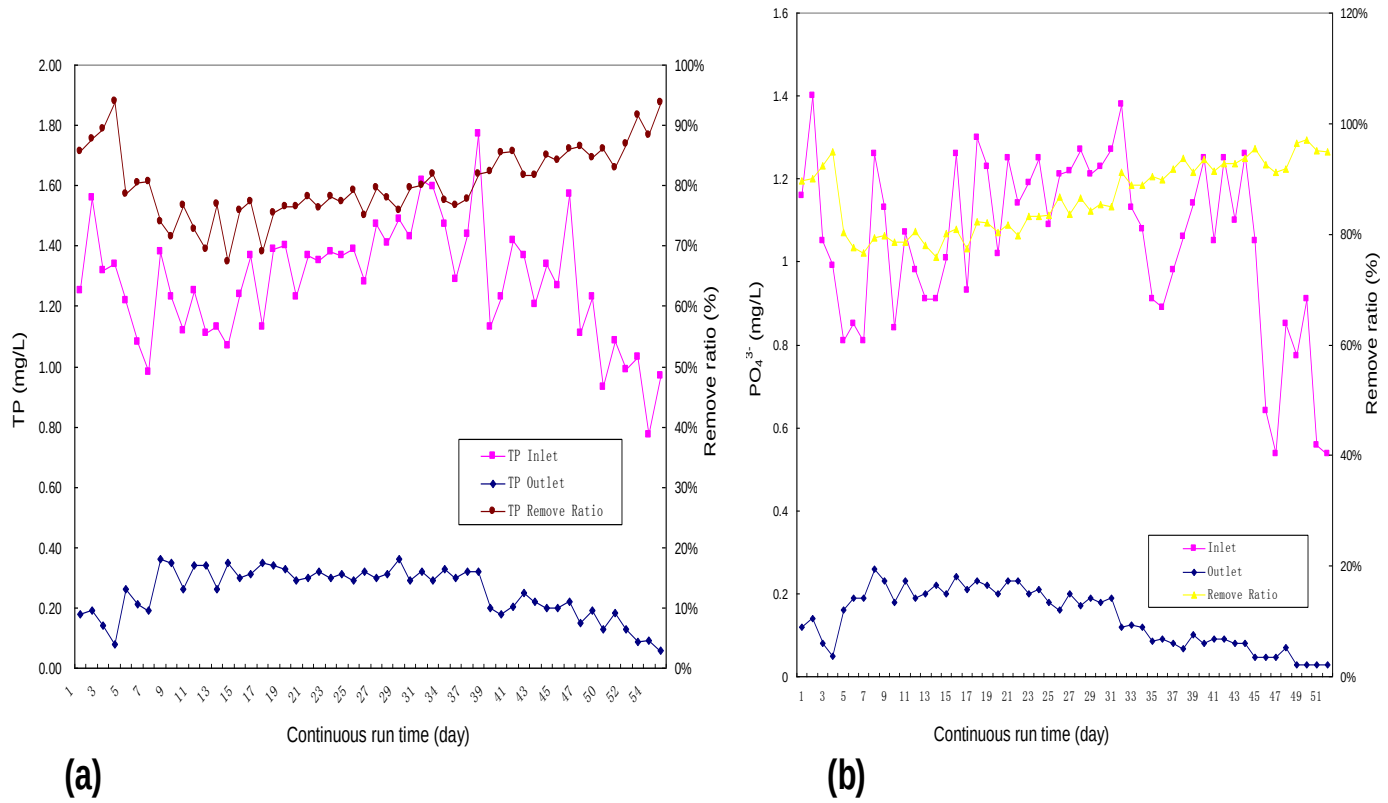

Figure 5. TP removal (a) and PO_4^{3-} removal (b) performance in constructed wetland with fly ash ceramsite II as the substrate.

Table 2. Single-level dynamic process for fly ash ceramsite adsorption of P.

Fly ash ceramsite	Temperature (°C)	Maximum P adsorption capacity	Single - level dynamic model		
		q_{max}	A	k_1 (h^{-1})	r^2
Number I	15	0.1362	0.1007	0.0830	0.8702
	20	0.1736	0.1610	0.0208	0.8943
	25	0.1874	0.1710	0.0257	0.8566
Number II	15	0.1142	0.1092	0.0125	0.9044
	20	0.1193	0.1109	0.0196	0.8609
	25	0.1293	0.1208	0.0179	0.8528

which is the maximum P adsorption capacity by fly ash ceramsite (mg kg^{-1}).

The results of physical and chemical properties, and test results of P adsorption capacity, show that fly ash ceramsite Number I was suited as the substrate for the continuous experiment in the constructed wetland to enhance P-removal.

Continuous experiment on fly ash ceramsite-assisted P removal in a constructed wetland

Fly ash ceramsite Number I was applied to the constructed wetland as substrate for removal of PO_4^{3-} and TP from contaminated water in the experiments below. The concentration of PO_4^{3-} and TP of influent stable at 0.10–0.40 and 0.01–0.22 mg·L^{-1}. In the first three days of continuous running, the P - removal rate of the device had an increasing trend, the TP removal rate reached 94.03% and PO_4^{3-} removal rate reached 94.95%, then the removal rate started to decrease gradually, but remained >70%. With further run time of the experiment, the removal rate gradually increased and reached 90% in the end.

The removal of P using a substrate in constructed wetland involves physical adsorption, chemical reaction and microbial degradation. PO_4^{3-} can react easily with metal ions (example, Fe^{3+}, Al^{3+} and Ca^{2+}) or be assimilated by aquatic plants or separated from water. Organic P can be adsorbed to the substrate by physical action and then be degraded by P bacteria, thus, being separated from the water. Combining the result of this experiment with the result of the static experiment done with fly ash ceramsite implies that the higher removal rate of the initial operation in constructed wetland depended on the high capacity of fly ash ceramsite for P adsorption, driven by physical adsorption and chemical adsorption (Ozacar, 2003). The capacity for physical adsorption is small, and easily saturated, whereas the chemical adsorption as a result of these elements (that is, mainly Al, Fe and Ca) react with P and so is more stable. In the initial run time, the P adsorption by the fly ash ceramsite was mainly physical and on the surface. However, with the gradual saturation of physical adsorption, chemical adsorption became the primary factor in TP removal, which gradually stabilized around 80%. As the experiment continued, microorganisms started to multiply in the substrate's internal spaces.

The increase in P-removal rate later in the experiment may be for two reasons: the participation of microbial P-removal and the development of plant root systems which assimilate P. The developed root system had other functions conducive for the growth of a large number of microorganisms including the supply of oxygen transported through leaf, stem and root. Aerobic conditions existed around the root zone but there were hypoxic and anaerobic (Schulz et al., 2003) conditions away from the root zone. This environment was conducive to P-bacteria degrading organic P into inorganic P, which can be assimilated by aquatic plants' roots. The effect of bacteria would then be to restore some physical adsorption capacity of the fly ash ceramsite.

During the 7 days of continuous operation, the removal rate of TP and PO_4^{3-} gradually increased along the constructed wetland (Figure 6), but the main removal was within the first two frames. The TP and PO_4^{3-} removal rates reached 80% before flowing into the third frame, in which the removal rate increased slightly. The adsorption capacity of the first two frames of constructed wetland should ensure the removal of P in sewage. Compared with traditional substrates, fly ash ceramsite had a larger P capacity and achieved a higher removal rate, which could reduce the size of the constructed wetland needed in any area. This is a positive contribution to wastewater treatment in the environment.

Conclusion

(1) The physical and chemical properties of two types of fly ash ceramsites were characterized by scanning electron microscopy and energy dispersive spectroscopy SEM/EDS. Both types of fly ash ceramsites showed porous structures with rough surfaces. However, compared to fly ash ceramsite Number II, Number I had a higher Ca content (that is, 23.16%) and rougher internal structure.

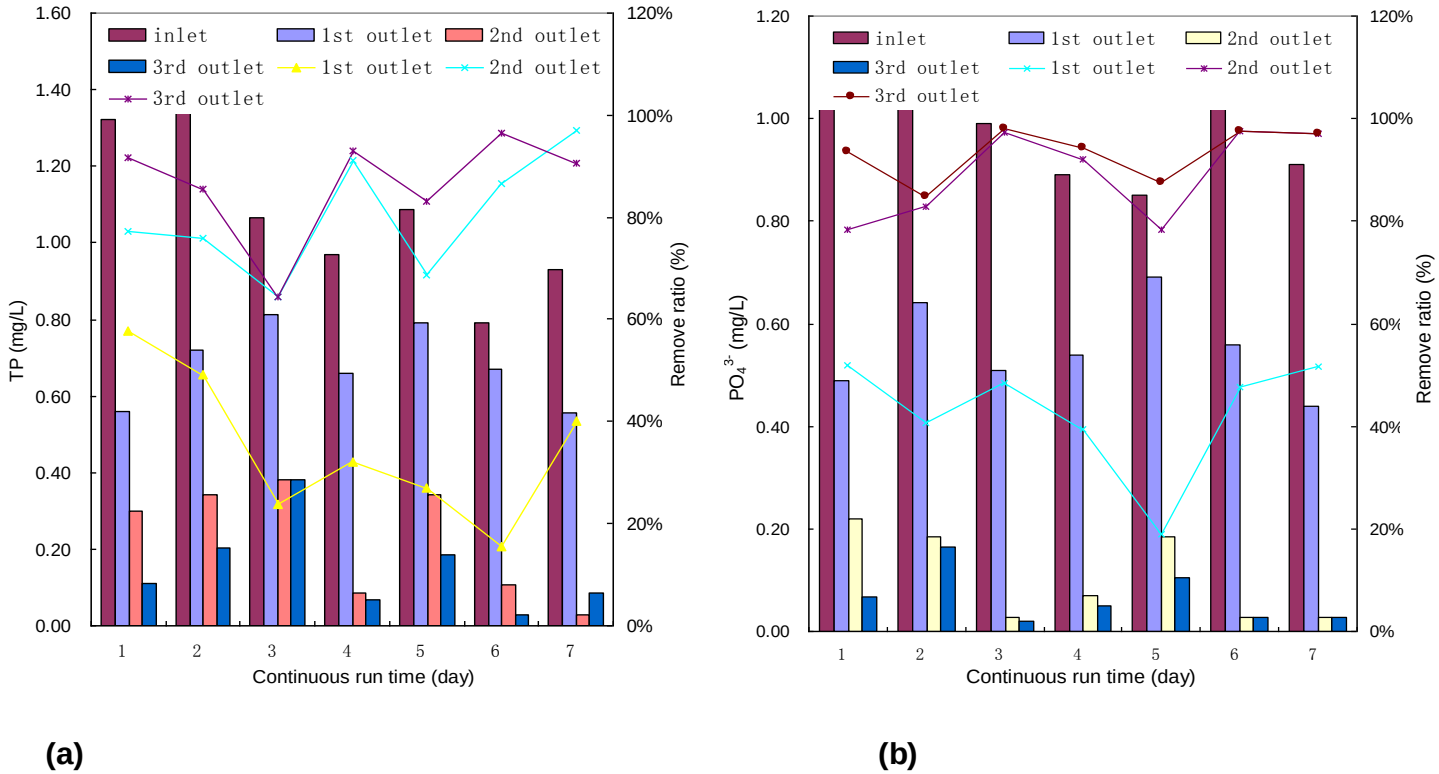

Figure 6. TP removal (a) and PO_4^{3-} removal (b) performance along a constructed wetland with Lgtag II as the substrate.

(2) The static experiment on PO_4^{3-} adsorption by fly ash ceramsite showed that their adsorption characteristics obeyed the Langmuir isotherm equation. The maximum P adsorption capacity was 0.892 and 0.597 mg g^{-1} for fly ash ceramsite Numbers I and II, respectively. In both cases, it took 3 h to reach adsorption equilibrium, and the adsorption processes could be described by a single-level kinetic model.

(3) The continuous experiment on P-removal using fly ash ceramsite in a constructed wetland demonstrated that fly ash ceramsite was compatible with the environment and significantly improved the physical and chemical treatment effects. The TP and PO_4^{3-} concentrations in the effluent after treatment were stable at 0.10 to 0.40 and 0.01 to 0.22 mgL^{-1}, respectively, and their removal rate reached 90%.

The present results indicate that fly ash ceramsite can be employed as a high-efficiency substrate in constructed wetlands to enhance P removal, and this can reduce the area required for constructed wetlands.

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REFERENCES

Brix H, Arias CA, Bubba M (2001). Media selection for sustainable phosphorus removal in subsurface flow constructed wetland. Sci Technol 44: 47-54.

Ham J, Yoon CG, Kim H-J, Kim H-C (2010). Modeling the effects of constructed wetland on nonpoint source pollution control and reservoir water quality improvement, J. Environ. Sci .22: 834-839

Li W, Zeng P (2009) .Constructed Wetland Wastewater Treatment Technology, China Water Power Press.

Ozacar M (2003) .Equilibrium and kinetic modeling of adsorption of phosphorus on calcined alunite. Adsorption, 9: 125-132.

Schulz C, Gelbrecht J, Rennert B (2003). Treatment of rainbow trout farm effluents in constructed wetland with emergent plants and subsurface horizontal flow. Aquaculture, 217: 207-221.

Song Z, Zhao B (2006). Organic matter removal efficacy and dynamic feature of constructed wetland for sewage treatment. Ecol. Environ. 15: 15-19.

Standard Method for the Examination of Water and Wastewater. Editorial Board, Beijing (2002). China Environ. Sci. pp. 243-246.

Xiang H, Li D (2006). Application of fly ash fly ash ceramsite in wastewater treatment. J Liaoning Technol Univ 25: 291-292.

Yuan DH, Jing L (2005). Analysis on the removal efficiency of phosphorus in some substrates used in constructed wetland systems. Environ. Sci. 26: 51-55.

Zhao G, Zhou Q (2007). Adsorption of phosphate on shale granules. Environ Pollut Cont 29: 182-185.

Zhu L, Zhu Z (2000) .Study of water treatment filter material: light global ceramsite. Environ. Prot. 1: 35-37 Water Treat 33: 18-20.