EnvironmentAsia
The international journal published by the Thai Society of Higher Education Institutes on Environment

Available online at www.tshe.org/EA
EnvironmentAsia 6(1) (2013) 60-65

Phosphorus Sorption Capacity of Concrete Waste, Natural Sorbents, Alum Residuals from Water Supply Sludge, and Ceramic Material for Tertiary Treatment in Onsite Systems

Siriporn Larpkiattaworn [a], Nut Pookerdsin [b], Mathurot Wangchanachai [b] and Pongsak Noophan [b]

[a] *Materials Innovation Department, Thailand Institute of Scientific and Technological Research Pathum-Thanee, Thailand*

[b] *Department of Environmental Engineering, Faculty of Engineering, Kasetsart University, Bangkok, Thailand*

Abstract

The phosphorus (P) sorption capacity was determined for concrete waste, alum residuals from water treatment sludge, and natural sorbents (shells, clay, kaolin, and mordenite) from various parts of Thailand. The material showing the best P sorption capacity (shells) was selected for preparing a ceramic material to support the growth of nitrifying bacteria. The ceramic material, consisting of shells (50% by weight), alum residuals sludge (40% by weight) and a soil (10% by weight) heat at 750°C for about one hour, was studied for its P sorption capacity. Langmuir and Freundlich sorption isotherms yielded similar relative maximum P sorption capacities for the sorbents. The results from the Langmuir calculations showed the following maximum P sorption capacities: 32.26 g P/Kg shells, 31.25 g P/Kg concrete waste, 7.19 g P/Kg alum residuals sludge, 290 mg P/Kg clay, 80 mg P/Kg kaolin, and 30 mg P/Kg mordenite. The P sorption capacity for the prepared ceramic material at grain size 12 mm was 4.85 g P/kg. This result suggests that the ceramic material could be used for P sorption while providing growth support for nitrifying bacteria, similar to the well documented a popular P sorption material: light expanded clay aggregate (LECA) from Sweden.

Keywords: phosphorus sorption; concrete waste; shells; alum residuals from water treatment sludge; clay; kaolin; mordenite; ceramic material

1. Introduction

Although phosphorus (P) is an essential nutrient for normal functioning of ecosystems, excess P as well as nitrogen (N) can stimulate eutrophication of freshwater lakes may contribute to the reduction of dissolved oxygen (DO), and can cause ecosystem perturbation in coastal zones. Furthermore, some N forms, e.g. nitrate (NO_3^-) is a potential public health hazard in drinking water because it increases the risks of methemoglobinemia (blue baby syndrome) in infants (Johnson and Kross, 1990). Nitrite (NO_2^-) is also affect to aquatic life. For these reasons, to prevent harmful effects on human health and aquatic life, P and N must often be removed from wastewaters before discharge into the environment.

In Thailand, as in many locations worldwide, domestic wastewater is commonly treated in conventional septic tanks, as opposed to central treatment plants. These small scale units alone cannot remove P and N to satisfactory levels. Theoretically, individual and onsite treatment systems (e.g. septic tank) are able to remove some organic matters (biochemical oxygen demand, BOD), P, and N by about 40-50%, 10-20%, and 10-15%, respectively (Crites and Tchobanoglous, 1998; U.S. EAP, 2002). Under some conditions both P and N pollutants in septic tank effluent (STE) can be discharged directly to the groundwater or freshwater. But often STE should be further treated prior to release.

Highly efficiency treatment systems have been developed but these are expensive to build and difficult to operate. Generally, removal of both P and N from wastewater by using only biological treatment is not simply and highly efficient because bacteria cannot change P into a gas phase as they can with N. An inexpensive and simple approach to remove P from STE with secondary treatment is by sorption and precipitation. Also, it would be quite beneficial to find an efficient P sorbent that would provide growth medium for N removing bacteria. Such an application to domestic sewage from STE is proposed by Katers and Zanoni (1998).

There are many P sorption studies in the literature including the following: Vohla *et al*. (2011) and Westholm (2006) determined the P sorption capacities for many materials. Johnsson (1997) reported that lightweight aggregates or light expanded clay aggregate (LECA) from Sweden had P sorption capacity of 12 g P/Kg for grain size 4 mm and 4.8 g P/Kg for grain size 10 mm. Zhu *et al*. (1997) reported that Utelite from Utah, USA could adsorb P at 3.46 g P/Kg and also be used as a growth medium for nitrogen removing nitrifying bacteria. Sakadevan and Bavor (1998) showed that a blast furnace slag from Australian Steel Mills Limited and the clinoptilolite material (Zeolite) could adsorb P at 44.2 g P/Kg and 2.15 g P/Kg, respectively.

In this investigation, sorbents from urban and rural area in Thailand were considered by following three main factors: availability, low cost, and source (preference for waste material of bypass product from some process). Thus, the following sorbents were selected for determination of P sorption capacity: concrete waste, alum residuals from water supply sludge, and natural sorbents (shells, clay, kaolin, and mordenite). Next, the sorbent having the highest P sorption capacity (shells) was blended with alum residuals from water treatment sludge and a soil heat at 750°C for about one hour. The resulting ceramic material was evaluated for its ability to adsorb P while supporting N removing nitrifying bacteria. For both criteria the ceramic material is comparable to light expended clay aggregate (LECA). The ceramic material from this work could be used in small or onsite wastewater treatment systems to improve P and N removal. This supporting growth media might be used in a unit operation of other wastewater treatment systems to enhance nutrients removal (tertiary treatment).

1.1. Sorbents

Concrete waste

Concrete is used for the construction of a large number and variety of structures worldwide because concrete is so stable, its disposal is often difficult. The most common methods for disposal include open dumping, landfill, and recycling. The composition of concrete waste is Ca (21.9%), Si (8.27%), Al (4.58%), O (53.51%), and C (11.74%). Concrete waste could be a good P sorption material because of high calcium. Its use in water treatment could reduce the environmental impact of concrete waste, making it much more eco-friendly.

Shells

In Thailand shells are waste from seafood industry and are plentiful along the coasts in the southern part of Thailand. In general, this material consists of high concentrations of Ca and Mg carbonates. The composition of shells in this study was Ca (27.66%), Al (6.41%), O (52.51%), and C (13.42%). Shells are another good source to use as a P sorption because of high Ca carbonate.

Natural sorbents

Natural sorbents, in this work (clay, kaolin, and mordenite) are found in various parts of Thailand. In general, the major components of these materials are Al, Fe or Ca. Although information about natural sorbents in some area or country is available, more research is needed to quantify the compositions of natural sorbents which could vary with location. Furthermore, the mechanism for P removal with natural sorbents is not well understood.

Alum Residuals from Water Supply Sludge

Alum residuals from water supply sludge are a waste that is generated during the flocculation/coagulation and sedimentation processes in a drinking water treatment plant. Alum residuals in this work were collected from the largest water supply treatment plant in Bangkok, Thailand. The compositions of alum residuals from water supply sludge at this plant are Al (17.02% by weight), Si (25.57% by weight), K (1.48% by weight), and Fe (7.43% by weight).

1.2. Langmuir and Freundlich Isotherm

The Langmuir isotherm based on equilibrium between sorption and de-sorption of phosphorus molecules is written

$$\frac{C_e}{Q} = \frac{1}{bK_1} + \frac{1}{K_1}(C_e) \tag{1}$$

where $Q = \frac{X}{M}$ is P adsorbed per unit weight of sorbents, C_e is equilibrium solution concentration, K_l is designated as the Langmuir sorption maximum, and b is related to binding energy. The Langmuir sorption maximum is calculated from the slope and intercept obtained by plotting C_e as x-axis against as $\frac{C_e}{X/M}$ y-axis.

The Freundlich isotherm is expressed as:

$$Q = KC^{1/n}, (n > 1) \tag{2}$$

where K and n are constants. The constant K is considered a hypothetical index of P absorbed from a solution having a unit equilibrium P concentration. This K could be used to relate P sorption capacity of the material.

2. Materials and Methods

2.1. Experimental Approach

In the initial work all sorbents: concrete waste, alum residuals from water treatment sludge, and natural sorbents (shells, clay, kaolin, and mordenite) were used at 0.05 mm grain size. Later, the mixture synthetic or called as the ceramic material (shells, 50% by weight, alum residuals from water treatment sludge, 40% by weight, a soil, 10% by weight and heat at 750°C for about one hour) was studied at 12 mm grain size (optimum size for support of nitrifying bacteria). A maximum of one gram of each sorbent was equilibrated in a 100 ml glass flask with 30 ml of 0.01 KCl solution containing various amounts of K_2HPO_4 ranging from 0 to 100 mg P/L. Flasks were shaken in a standard shaker (100 rpm) for 48 hours at normal room temperature (25ºC). The decrease in P from the aqueous solution was assumed to have been adsorbed by sorbents. Phosphate adsorbed per unit weight (dry weight) of all sorbents was used to fit Langmuir and Freundlich sorption isotherm equations.

To evaluate the efficacy of the synthetic ceramic material for P sorption and nitrifying bacterial growth support, a trickling filter apparatus was assembled using a cylinder 2.4 cm dimensions and 18 cm height. The synthetic ceramic material was added to a depth of 15 cm. Air was allowed to flow through from top to bottom of the cylinder. An enriched, mixed nitrifying culture from the activated sludge of a municipal centralized wastewater treatment plants in Bangkok, Thailand was used to inoculate the material. The liquid feed was a synthetic solution prepared with tap water, ammonium sulfate (30-45 mg N/L), bicarbonate (200-250 mg/L as $CaCO_3$) and nutrients. The pH of feed solution was varied from 8.4 to 8.5. A Chron-Trol programmable controller was used to control the pump feeding the synthetic solution to the trickling filter (every 3 minute).

2.2. Orthophosphate Measurement

Aqueous orthophosphate P content remaining in solution was measured by colorimetric methods as described by Andrew (1995) in Standard Methods for the Examination of Water and Wastewater (1998). About 25-30% of samples were randomly selected and analyzed by ion chromatograph (761 Compact Ion Chromatograph, IC, Methrom, Herisau, Switzerland). The results from the IC analysis were compared with the results from the colorimetric method. Results were not significantly different, demonstrating the appropriateness of the colorimetric method used throughout this work.

2.3. Surface Area and Chemical Characteristics of Sorption Materials

Surface area of concrete waste, shells, and alum residuals from water treatment sludge was analyzed by Brunauer Emmett Teller (BET), Quantachrome Model Autosorb-1 (single-point and multi-point). The chemical characteristics of concrete waste, shells, and alum residuals from water treatment sludge were analyze by Energy Disperive X-ray Spectrometer, Jeol Model JSM-6340F.

3. Results and Discussion

P sorption data from all sorbents were used to fit both Langmuir and Freundlich sorption isotherms, as shown in Table 1.

The chemical characteristics and surface area of all sorption materials: shells, concrete waste, and alum residuals sludge are shown in Table 2.

As shown in Table 1, the relative P sorption maxima for the sorbents tested are the same using Langmuir or Freundlich isotherm calculations. Because the Langmuir results provided higher least square fit values (R^2), they were used to determine maximum P sorption capacities. The concentration of P in the equilibrium solution was

Table 1. Coefficients of Langmuir and Freundlich isotherms for concrete waste, alum residuals from water treatment sludge and all natural materials: shells, clay, kaolin, and mordenite

		Langmuir	**isotherm**		**Freundlich**	**isotherm**
Material	R^2	**Sorption-maximum (g P/Kg)**	**Binding energy (L/g)**	R^2	**Hypothetical index of P sorb (g P/Kg)**	**n**
Shells	0.99	32.26	0.517	0.97	18.15	7.14
Concrete waste	0.90	31.25	0.136	0.61	14.32	6.67
Alum residuals from water treatment sludge	0.80	7.19	0.023	0.72	0.418	1.77
Clay	0.99	0.29	21.82	0.98	0.031	1.79
Kaolin	0.99	0.08	9.2	0.98	0.016	2.29
Mordenite	0.82	0.03	4.8	0.82	0.008	2.52

Table 2. Chemical Characteristics and Surface Area of Shells, Concrete Waste, and Alum Residuals Sludge

Material	Element (weight %)							BET (m^2/g)
	C	Al	Si	Ca	K	Fe	O	
Shells	13.42	6.41	-	27.66	-	-	52.51	2.846
Concrete waste	11.74	4.58	8.27	21.90	-	-	53.51	2.828
Alum residuals sludge	-	17.02	25.57	1.48	1.25	7.43	47.25	52.54

related to P sorption of shells, concrete waste, and alum residuals from water sludge by using Langmuir equation shown in Fig. 1. Shells showed the highest P sorption capacity at 32.26 g P/Kg shells. Previously Roseth (2000) reported the maximum P sorption capacity of shell sand at 14-17 g P/Kg, lower than the value found in the current study. The difference could be attributed to Roseth's using a mixture of shells, snails and coral alga. This study used only shells. Typical shells chemical characteristics from this study are Ca (27.66%), Al (6.41%), O (52.51%), and C (13.42%) and surface area by BET is 2.846 m^2/g. Roseth's work reported the composition, only carbonatic material. The P sorption capacities of concrete waste and alum residuals from water supply sludge were 31.25 g P/Kg and 7.19 g P/Kg, respectively. Although in the literature review there were many experiments which used concrete waste to remove P, the reports of P sorption capacity were not available. This study firstly reported the P sorption capacity and analysis of the composition of concrete waste. The chemical characteristics of concrete waste are Ca (21.9%), Si (8.27%), Al (4.58%), O (53.51%), and C (11.74%). A high Ca carbonate is mainly composition of concrete waste. The binding energy of concrete waste is lower than the binding energy from shells. Blinding energy is another important parameter in P sorption. For these reasons, shells were used to be a main of mixture in ceramic material.

The P sorption of alum residuals from this work was comparison with literature review. Martula and Gagnon (2007) reported that the Langmuir isotherm in P sorption capacity on alum residuals in their work was 7.11 g P/Kg. The chemical characteristics of alum residuals from water treatment sludge in this study are Al (17.02% by weight), Si (25.57% by weight), K (1.48% by weight), and Fe (7.43% by weight). The surface area of alum residuals from water treatment sludge by BET is 52.54 m^2/g. There is a high surface area comparison with other material. The occurrence of Al and Fe compositions in alum residuals from water treatment sludge could be significantly increased P removal in both sorption and precipitation processes. For these reasons, alum residuals from water treatment sludge were used to be a one of mixture in ceramic material.

The concentration of P in the equilibrium solution was related to P sorption of clay, kaolin, and mordenite

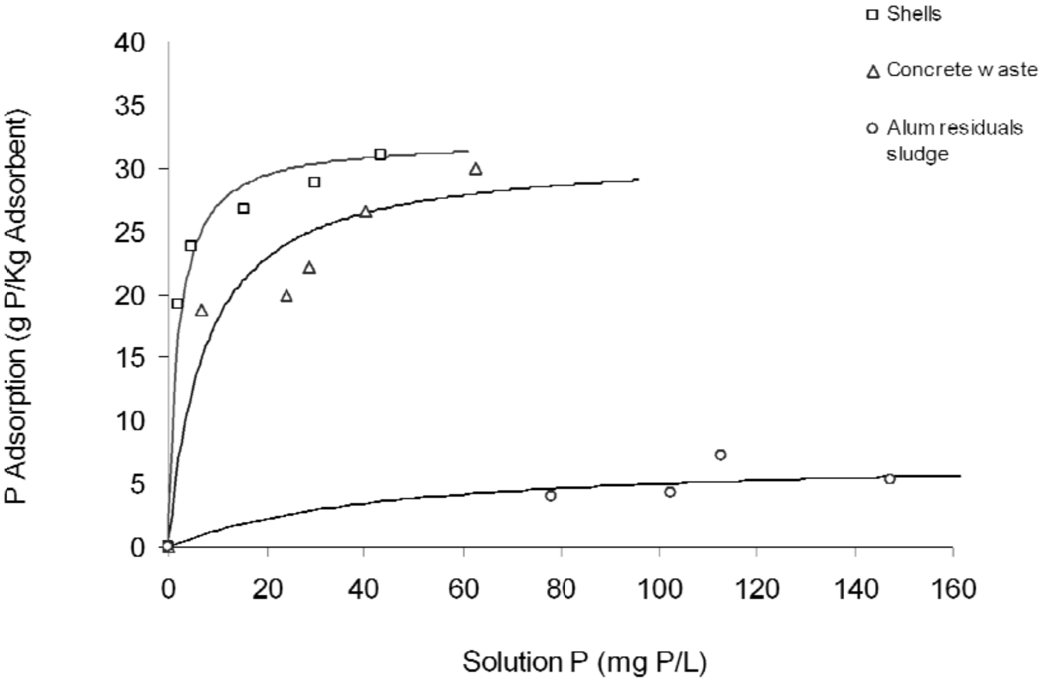

Figure 1. Phosphorus sorption vs. equilibrium solution P for shells, concrete waste, and alum residuals from water treatment sludge by using Langmiur equation

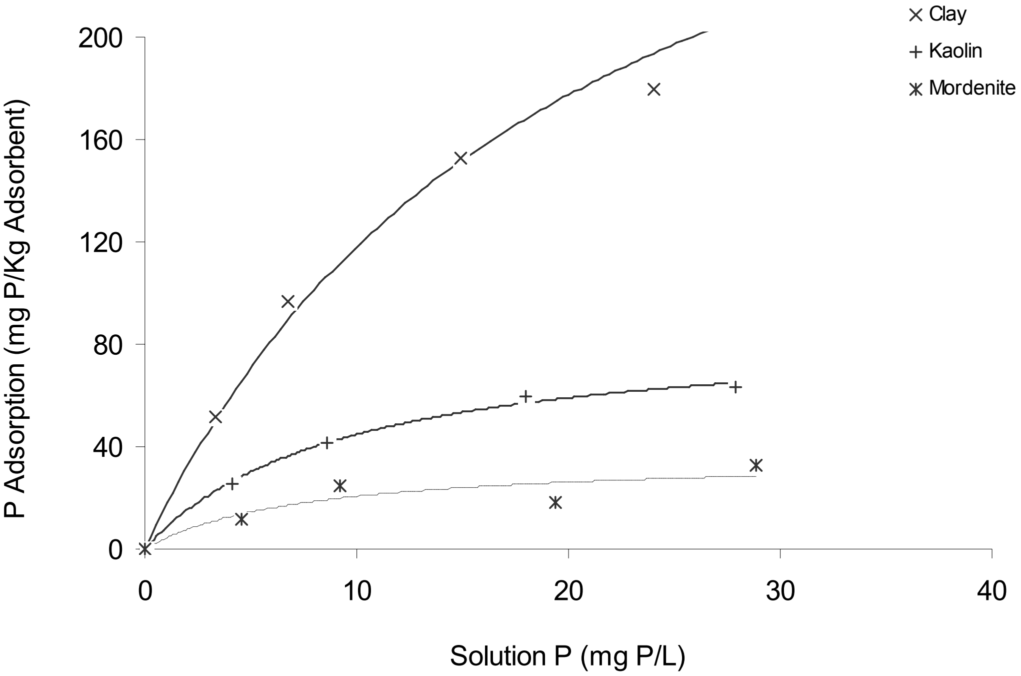

Figure 2. Phosphorus sorption vs. equilibrium solution P for clay, kaolin, and mordenite by using Langmiur equation

by using Langmuir equation shown in Fig. 2. Clay, kaolin, and mordenite had slightly to lower capacities of 290 mg P/Kg clay, 80 mg P/Kg Kaolin, and 30 mg P/Kg Mordenite, respectively. However, P sorption capacity of clay was significantly higher than P sorption capacity of sand 50 times. Aulenbach and Meisheng (1988) reported that P sorption capacity of sand 5.6 mg P/Kg.

Although ground shells provide very high P sorption capacity, they cannot be applied directly in the field because of the very fine grain size (0.3 mm). Nitrifying bacteria would not be expected to grow well on this material because of the limited oxygen concentration. A simple method for increasing grain size was to blend ground shells (50% by weight), alum residuals from water supply sludge (40% by weight) with a soil (10% by weight) and heat at 750°C for about one hour. This mixture was called as the ceramic material. The resulting of ceramic material had a grain size 10-12 mm, pervious shown to promote the growth of nitrifying biofilms. Over a period of several weeks, it was demonstrated that nitrifying bacteria

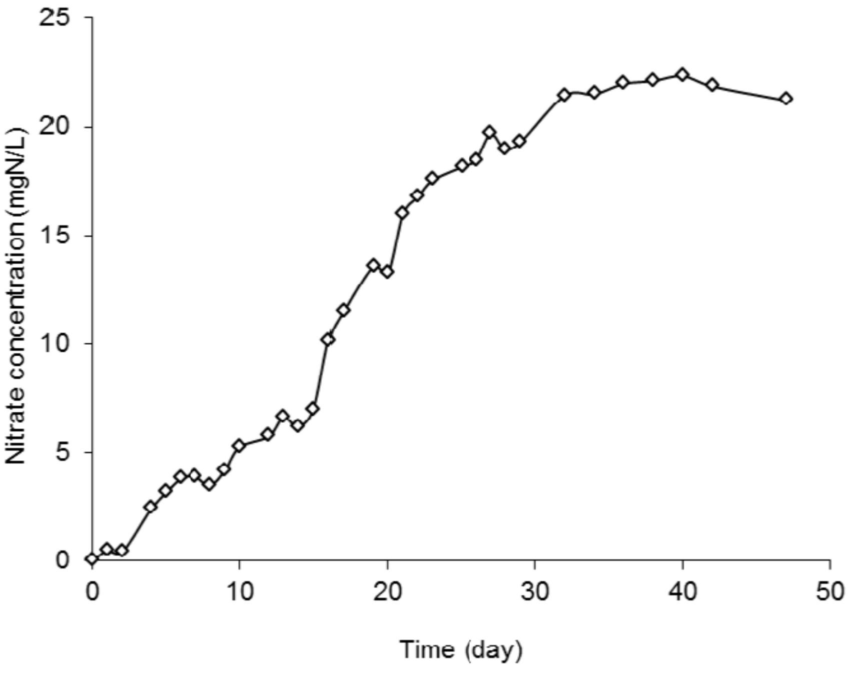

Figure 3. Nitrate concentration vs. time during nitrification process by using ceramic material as a medium

associated with the synthetic blend or ceramic material significantly oxidized ammonium (NH_4^+) to nitrate (NO_3^-) as show in Fig. 3.

The ceramic material was also tested for P sorption capacity by the Langmuir equation. The maximum P sorption of this ceramic material was 4.85 g P/Kg. In previous research by Johansson (1997) and Oovel *et al*. (2007), it was shown that nitrifying bacteria were supported by coarse media (grain size 10 mm) such as light expanded clay aggregate (LECA). The coarse media had significant water permeability and good P sorption (4.8 g P/Kg LECA). The ceramic sorbent material prepared in this work had a comparable P sorption capacity (4.85 g P/Kg ceramic sorbent material). Moreover, this ceramic material could be used as a material for nitrifying bacteria for removal N. It is suggested that this ceramic material could be used within individual wastewater treatment systems, such as a medium in trickling filter, infiltration trench, and constructed wetlands.

4. Conclusion

Shells provided the highest P sorption capacity as compared with all other tested sorbents. P sorption capacities for clay, kaolin, and mordenite are quite low. A ceramic material with a larger grain size (12 mm) was prepared with ground shells, alum residuals from water treatment sludge, and a soil. The ceramic material could be use in wastewater treatment as a biomass growth support for nitrifying bacterial well, while providing P sorption capacity of 4.85 g P/Kg. The synthetic mixture or ceramic material compares favorably with LECA from Sweden with respect to both P sorption capacity and a nitrifying bacteria growth support. The ceramic material from this study could be used in the tertiary treatment in onsite wastewater treatment.

Acknowledgements

The authors express their thanks to the Thailand Institute of Scientific and Technological Research Pathum-Thanee, Thailand for providing a grant for this research and to the Center of Advanced Studied in Industrial Technology, Faculty of Engineering, Kasetsart University Bangkok, Thailand for strong support through this project. The authors also thank Metropolitan Waterworks Authority, Bangkok, Thailand for providing the water treatment sludge.

References

APHA. Standard Methods for the Examination of Water and Wastewater. 20th ed. APHA, AWWA, WPCF, Washington, DC, USA. 1998; 135-41.

Aulenbach DB, Meisheng N. Studies on the Mechanism of Phosphorus Removal from Treated Wastewater by Sand. Journal of Water Pollution Control Federal 1988; 60 (12): 2089-94.

Crites RW. Tchobanoglous G. Small and Decentralized Wastewater Management Systems. McGraw-Hill Publishing Company., Boston, USA. 1998; 920-26.

Johansson L. The use of LECA (Light Expanded Clay Aggregates) for the Removal of Phosphorus from Wastewater. Water Science and Technology 1997; 35: 87-93.

Johnson CJ, Kross BC. Continuing Importance of Nitrate Contamination of Groundwater and Wells in Rural Areas. American Journal Industrial Medicine 1990; 180: 450-56.

Katers JF, Zanoni A E. Nitrogen Removal (a lab-scale checks the effectiveness of a modified septic tank in reducing nitrogen discharge). Water Environment and Technology 1998; March, 32-36.

Mortula MM, Gagnon GA. Alum Residuals as a Low Technology for Phosphorus Removal from Aquaculture Processing Water. Aquacultural Engineering 2007; 36: 233-38.

Oovel M, Tooming A, Mauring T, Mander U. Schoolhouse Wastewater Purification in a LWa Filled Hybrid Constructed Wetland in Estonia. Ecological Engineering 2007; 29: 17-26.

Roseth R. Shell Sand: A New Filter Medium for Constructed Wetlands and Wastewater Treatment. Journal of Environmental Science and Health Part A 2000; 35 (8): 1335-55.

Sakadevan K, Bavor HJ. Phosphate Sorption Characteristics of Soils, Slags and Zeolite to be Used as Substrates in Constructed Wetland Systems. Water Research 1998; 32 (2): 393-99.

U.S. EPA Onsite Wastewater Treatment Systems Manual. EPS/625/R-00/008. February 2002. Office of Research and Development 2002; 4-37-40

Vohla C, Koiv M, Bavor HJ, Chazarenc F, Mander U. Filter Materials for Phosphorus Removal from Wastewater in Treatment Wetlands-A Review. Ecological Engineering 2011; 37: 70-89.

Westholm, LJ. Substracts for Phosphorus Removal- Potential Benefits for On-site Wastewater Treatment. Water Research 2006; 40: 23-36.

Zhu T, Jenssen PD, Maehlum T, Krogstad T. Phosphorus Sorption and Chemical Characteristics of Light Weight Aggregates (LWA)-Potential Filter Media in Treatment Wetlands Water. Science and Technology 1997; 35 (5): 103-08.

Received 18 October 2012
Accepted 30 October 2012

Correspondence to
Dr. Pongsak Noophan
Department of Environmental Engineering,
Faculty of Engineering,
Kasetsart University,
50 Ngam Wong Wan Road, Chatuchak,
Bangkok, 10900
Thailand
Email: pongsak.n@ku.ac.th