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Phosphorus retention capacity of filter media for estimating the longevity of constructed wetland

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Abstract

The filter medium could be selected and the longevity of the filter medium by the phosphorus saturation could be predicted in the constructed wetland system, accordingly proposing the scheme to remove the phosphorus for a long period. The phosphorus adsorption capacities of various filter media were investigated in relation to the size and types of filter media to screen the optimal condition. The objective of this study was to evaluate the constructed wetland longevity by improving P adsorption capacity. The maximum P adsorption capacities of filter media A (4–10 mm), B (2–4 mm), and C (0.1–2 mm) were 7.7, 11.6, and 22.5 mg/kg, respectively, showing that they increased as the filter media size decreased. Among the experimental media, the optimal filter media size was 0.1–2 mm. When Ca, Mg, Al and Fe were added to the filter medium C, which is the optimal filter medium, the addition of Ca improved mostly the P adsorption capacity. In the alternative proposal to use these facts, the oyster shell was added to the filter medium and the P adsorption capacity was examined: adding 2% oyster shell increased the P adsorption capacity from 23 to 36 mg/kg. In the column where the oyster shell was mixed, when the oyster shell content was 5%, 10%, 20%, 40%, 60%, 80%, and 100% in the filter medium C, the respective saturation times of the P adsorption were about 6, 9, 17, 30, 43, 56, and 70 days. When the oyster shell content was 0%, 5%, 10%, 20%, 40%, 60%, 80%, and 100% after 1 month in the column, the P adsorption amount was about 180, 600, 1560, 4280, 6157, 7089, 7519, and 7925 mg/kg, respectively. The increment of the P adsorption amount was small if the oyster shell content was 60% or more, because the filter medium with more than 60% oyster shell content did not approach the saturation time by the P adsorption yet. The P adsorption amount for 60%, 80%, and 100% could be predicted as about 9702, 12,879, and 16,056 mg/kg, respectively. The largest amount of extracted P in the filter media with oyster shell after 30 days of P solution application was bound to Ca, followed by water soluble-P, Al–P, and Fe–P. Therefore, it was concluded that the adsorption amount of the phosphorus could be increased by adding the oyster shell to the filter medium. Also, it was concluded that adding the oyster shell to the filter medium in the constructed wetland was the scheme to extend the longevity of the constructed wetland by the phosphorus saturation, and using the oyster shell would be useful in aspect of economical efficiency and

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easiness. Especially, it would be the alternative proposal to reduce the environmental pollution in aspect of recycling wastes.

Keywords: Phosphorus adsorption capacity; Constructed wetland; Langmuir isotherm; Filter media; Oyster shell; Phosphorus fractionation; Adsorption velocity

1. Introduction

The constructed wetlands are considered as low-cost alternatives for treating municipal, industrial and agricultural wastewater. Over the last 2 decades, several studies have reported on the potential use of wetlands for removal of nutrients, including phosphorus (P) from wastewater (Reddy and Smith, 1987; Mitsch and Cronk, 1992). The constructed wetland systems generally have a greater potential to remove nitrogen than phosphorus because nitrogen can be converted to nitrogen gas and be emitted to the atmosphere as a consequence of coupled nitrification–denitrification process. The only sustainable removal mechanism for phosphorus in the constructed wetland systems is plant uptake (Greenway and Woolley, 1999), accretions of wetland soils (Kadlec, 1997), microbial immobilization (Newbold et al., 1983; Reddy et al., 1999), retention by media (Tanner et al., 1998) and precipitation in the water column (Diazo et al., 1994). Since P is retained within the wetland, its ultimate removal from the constructed wetland system is achieved by harvesting plants and removing the saturated filter media. However, the amount of phosphorus that can be removed by harvesting plants usually constitutes only a small fraction of the amount of phosphorus loaded into the system with the sewage (Brix, 1994 and 1997). Phosphorus may also be bound to the media of the constructed wetland mainly as a consequence of adsorption and precipitation reactions with calcium (Ca), aluminum (Al) and iron (Fe) in the sand or gravel substrate (Gerrites, 1993). Adsorption and/or precipitation of P by a substrate in the constructed wetland systems are a finite process; once the material is saturated, it will have to be either washed or, more probably, replaced. Therefore, the P adsorption capacity of a material represents a central parameter for comparing and selecting candidate materials to be used as P removal media in the constructed wetland systems (Richardson and Craft, 1993; Mann, 1997; Johansson, 1999). However, the knowledge of P adsorption capacity of the material can be used to estimate the maximum amount of P that can be taken and/or removed from a given wastewater, while it cannot provide an accurate estimation of the longevity of a wastewater treatment system. Therefore, P batch experiments should be coupled with a long-term investigation of materials performed in columns for the estimation of P removal efficiencies and retention capacities by different materials. In addition, the longevity of the material to be used as a medium in constructed wetland systems is an important parameter for practical applications (Mann, 1997; Drizo et al., 1999; Johansson, 1999).

Many previous studies have been conducted to investigate the potential of various materials to remove P from wastewater. Various media including limestone, shale, slag, gravel, fly ash, blast furnace slag, light-expanded clay aggregates (LECA), and other artificial materials have been used in the constructed wetlands (Mann, 1997; Zhu et al., 1997; Drizo et al., 1997; Johansson, 1997) reported that shale-based constructed wetlands with or without reeds (*Phragmites australis*) have 98–100% P removal capacity. Blast furnace-slag (a by-product of limestone, coke, and iron ore), zeolite, and pelleted-clay either alone or in combination with soils (Sakadevan and Bavor, 1998), and alum, calcite, and dolomite (Ann et al., 1999) improve the P retention capacity of the constructed wetlands. More recently, the efficiency of wollastonite was studied in the US (Brooks et al., 2000) while several Danish sands, calcite, marble, vermiculite, and LECA were tested in Denmark (Arias et al., 2000). In Quebec, 57 materials were compared for their affinity to adsorb phosphorus, and it was found that electric arc furnace (EAF) steel slag has a high potential for P removal (Forget et al., 2001). The first criteria in selecting materials, tested in most of the above studies, were their chemical and physical properties such as Fe, Al, and Ca content; specific surface area; porosity; particle size distribution; and hydraulic conductivity, because they affect the rate and/or capacity of P adsorption (Richardson and Craft, 1993; Mann, 1997; Zhu et al., 1997). Although many filter media are used for the research on P adsorption capacity in the constructed wetland systems, most filter media are limited in aspect of economical efficiency and easiness to be applied to the actual site. Thus, the research for using sand has been considerably conducted. However, P adsorption capacity of sand is quite variable depending on local and/or physico-chemical features. Therefore, it is decided that the selection of the proper filter medium for actual local circumstances is mandatory. In particular, a new filter medium with excellent adsorption capacity should be selected to satisfy both economical efficiency and easiness. Therefore, oyster shell is used in this experiment, because it is estimated to satisfy the requirement of the new filter medium. Although treatment methods of phosphorus in water have been studied, there is no case applied to the constructed wetland system. Use of oyster shell will be the scheme to improve P adsorption capacity, recycle waste matters, and reduce environmental pollution. Especially, in Korea, a great quantity of oyster shells is generated as a by-product from the oyster culture in the south coast. The amount of oyster shell was about 0.25 million tons/year as of the late of 2003, of which only 10% was treated for oyster spat attachment (2000 tons/year) and fertilizer (2000 tons/year) (Ministry of Environment Republic of Korea, 2003). Most oyster shells are stocked in seashore, causing environmental problems such as polluting fishing places, giving difficulties to manage the public water surface, and damaging scenic beauty; thus, management or recycling of oyster shells is urgently required. Various physico-chemical properties (including pH and amorphous and poorly crystalline Al and Fe oxides) of these filter media influence the P sorption phenomena onto their surfaces (Reddy et al., 1999). The P adsorption capacity of materials was estimated by fitting the Langmuir or Freundlich isotherm equations to experimental data (Drizo et al., 1999; Zhu et al., 1997; Sakadevan and Bavor, 1998; Mann and Bavor, 1993). However, it was recently demonstrated that the Langmuir equation with such experimental data can lead to biased and unrealistic estimates of the adsorption parameters and should be used with caution for the applications of P adsorption studies to the constructed wetland systems. A need for establishing a new procedure for P batch experiments that would provide a more realistic comparison of the materials was recognized, and several criteria for this purpose were suggested (Forget et al., 2001; Drizo et al., 2000). In addition, it was recommended that P batch experiments should be coupled with a long-term investigation of materials performance in columns for the estimation of P removal efficiencies and retention capacities by different materials. The availability of data on the long-term performance of different materials in columns is limited (Johansson, 1999; Brooks et al., 2000; Baker et al., 1998). Moreover, the P saturation potential of the material (the point at which all of the available sites are saturated with P) was reported by only one study. This parameter is important because it enables us to estimate the duration of a full-scale system, if a specific material is going to be used in field application. When planning the design and construction of a wetland system to obtain efficient and cost-effective P removal, the longevity of the system is one of the major questions to address by the designer. Data from a long-term test, until it reaches P saturation, should provide a better estimate than batch tests of the long-term efficiency of the material (Drizo et al., 1999, 2002).

In the constructed wetland system, the filter medium could be selected and the longevity of the filter medium by the P saturation could be predicted, accordingly proposing the scheme to remove the phosphorus for a long period. Furthermore, the examination of the P adsorption velocity in the constructed wetland system will be the very significant factor to determine the depth and the hydraulic retention time (HRT) of the filter medium at the time of construction and design of the constructed wetland system.

In this paper, a filter medium for local environmental circumstances was selected in the constructed wetland system, and the oyster shell was examined to see the propriety to be used as a filter medium. First, the maximum P adsorption capacity per grain size of the filter medium for a short period was examined in batch experiment, and the optimum filter medium was selected according to the previous research methods in order to survey the P adsorption capacity, which is accumulated in the constructed wetland and reacts as the limit factor of the constructed wetland longevity. Also, the maximum P adsorption capacity was surveyed in order to inspect the scheme to extend the longevity of the constructed wetland by improving the P adsorption capacity, which reacts as a limit factor in the constructed wetland using the natural purification method, and to survey the possibility to use the plant organic matters and the oyster shells accumulated and corroded in the constructed wetland as an adsorbent. Based on the Batch experiment results, the P saturation period and the P adsorption amount were examined depending on the oyster shell content in the column experiment for a long period. Furthermore, the speed to eliminate phosphorus in the column depending on the oyster shell content was studied using a linear velocity equation, and the combination form of phosphorus was examined depending on the composition of the filter medium through the P fractionation of the filter medium where the oyster shell was mixed by the 1 month continuous injection of the phosphorus solution. Based on the above results, the propriety of the filter medium and the oyster shell were examined for the actual constructed wetland circumstances, and the scheme was suggested to remove the phosphorus in the constructed wetland system for a long period. Also, the longevity of the constructed wetland due to the saturation of phosphorus was predicted.

2. Materials and methods

2.1. Materials

The filter media used in the present investigation originated from the aggregate quarry in Namhae, in Korea. Three different filter media were used in the batch and column experiments and each filter medium type was available in three different particle sizes; 4–10, 2–4 and 0.1–2 mm. Therefore, the composition of filter media that is commercially available for use in the constructed wetland differs depending on the location of origin. The organic matters used in this study were corrosion water plants (*Phragmites communis* T_{RIN}, *Phragmites japonica* S_{TEUD}, *Carex dispalata* B_{OOTT}, and *Iris pseudoacorus* L.), products of constructed wetland. The oyster shell used to be neglected to the waste after oyster farming in Namhae seashore, Korea.

2.2. Characterization of materials

Chemical composition and physical properties of the materials, presented in Tables 1 and 2, were analyzed as follows: pH (1:5 water extraction), EC (1:5 water extraction), organic matter (Wakley and Black method), and T-N (Kjeldahl method). The concentration of P in the materials was measured by spectrophotometer (Beckman, DU 650 spectrophotometer, USA) after digestion in boiling H_2SO_4–$HClO_4$ ($n = 3$) according to the vanadomolybdate method of filter media analysis. The concentrations of Ca, Mg, Al, and Fe in the materials were analyzed by atomic absorption spectrophotometer (Shimadzu AA-680, Japan) after digestion in boiling H_2SO_4–$HClO_4$ ($n = 3$) according to the method of soil analysis (RDA, 1998).

The particle-size distribution of the filter media, organic matter, and oyster shell on a weight basis was analyzed in triplicate by conventional dry-sieving techniques. The grain-size distribution plots were used to estimate d_{10} (10% of the sand by weight is smaller than d_{10}) and d_{60} (60% of the sand by weight is smaller than d_{60}). The uniformity of the particle-size distribution (the uniformity coefficient) was calculated as the ratio of d_{60} to d_{10}. Porosities were determined from the amount of water, needed to saturate a known volume of sand ($n = 3$), and the bulk density of the filter media, organic matter and oyster shell (g/cm^3) was based on the ratio of the dry weight to the bulk volume of the filter media, organic matter, and oyster shell ($n = 3$). Saturated hydraulic conductivities were determined using the constant-head method ($n = 5$) in the laboratory.

2.3. Adsorption isotherm experiment

The maximum phosphate adsorption capacity was determined using a slightly modified batch equilibrium technique (Drizo et al., 1999, 2000) as described below. Nine P solutions, ranging from 0 to 320 mg of P/L (0, 2.5, 5, 10, 20, 40, 80, 160, and 320 mg of P/L, using KH_2PO_4 as P source) were tested. This wide range of P concentration was chosen to study the variability in P adsorption capacity and its dependence on the initial P concentration. Each test used 5–10 g of filter media, organic matter, and oyster shell, 10 g of filter media supplemented with different level of organic matter (0%, 0.5%, 1%, and 5%), and 10 g of filter media C supplemented with different level of Ca (0.01%, 0.05%, and 0.1%), Al (0.25%, 0.5%, and 1%), Fe (0.25%, 0.5%, and 1%) and oyster shell (0.5%, 1%, and 2%) in 250 mL glass Erlenmeyer flasks containing 100 mL of a P solution (KH_2PO_4 in distilled water), respectively.

The glass Erlenmeyer flasks were continuously shaken (175 rpm) on a 25 mm sway gyratory shaker for 24 h at laboratory temperature (20 °C). Blanks containing no materials were always included in the experiments. All experiments were conducted in triplicates. After settling, an aliquot of the supernatant was filtered through Whatman GF/C filters and after adequate dilution analyzed for phosphorus using the molybdenum blue-ascorbic acid method (APHA, 1995). The amount of phosphorus removed from solution by the filter media was calculated from the decrease in the solution P concentration.

The Langmuir equation, in its original form, can be written as

$$q = \frac{abC_e}{1 + aC_e}, \tag{1}$$

where C_e is the concentration of P in solution at equilibrium (mg/L), q is the mass of P adsorbed to the sand (mg/g), b is the apparent P-capacity (mg/g), and a

Table 1
Chemical characteristics of the filter media used

Materials	pH (1:5)	EC (1:5; dS/m)	O.M (g/kg)	T–N	T–P	Ca (mg/kg)	Mg	Al	Fe
Filter medium A	7.8	0.04	12.8	7.6	3.3	690	1458	1.19	1197
Filter medium B	7.9	0.05	7.9	8.5	2.1	790	215	1.94	765
Filter medium C	6.5	0.03	7.0	18.7	1.7	13	186	0.69	1321
Organic matter	6.8	2.13	501.6	12,030.0	10.2	27	1616	199.80	3382
Oyster shell	7.3	0.04	1.4	621.0	314.0	378,000	2200	0.23	610

Table 2
Physical characteristics of the filter media tested for P-removal properties

Materials	Porosity (%)	Bulk density (g/cm^3)	d_{10} (mm)	d_{60} (mm)	d_{60}/d_{10}	Ks (m/day)
Filter medium A	52	1.24	3.50	6.10	1.74	4320
Filter medium B	37	1.58	1.50	3.00	2.00	1234
Filter medium C	31	1.59	0.40	1.60	4.00	66
Organic matter	64	0.19	0.27	1.30	4.81	320
Oyster shell	57	0.83	0.90	1.50	1.66	1728

Values for porosity, d_{10}, d_{60} and the uniformity coefficient (d_{60}/d_{10}) are mean of triplicate analyses. Values for hydraulic conductivity (Ks) are means ± 1 SD ($n = 5$).

is a constant related to the binding strength of P. Linear regression analysis was performed on data where $C_e < 20$ mg/L and the inverse of the slope of the regression line calculated as a measure of apparent P-sorption capacity.

In linear form, Eq. (1) becomes

$$\frac{C_e}{q} = \frac{1}{b} C_e + \frac{1}{ab}, \quad (2)$$

which represents a straight line with slope $1/b$ and intercept $1/ab$ (DS, 1997).

Theoretically, Eq. (2) allows to estimate both the maximum adsorption (b) and the constant (a), which represents the inverse of the equilibrium concentration of adsorption at one-half saturation and gives; therefore, apparent P adsorption capacity of the filter media was estimated using the linear form of the Langmuir equation.

2.4. Column experiment

A total of 36 columns were constructed from column (i.d.: 21 mm, height: 365 mm) and each packed with 100 g of filter medium C supplemented with different oyster shell levels (0%, 5%, 10%, 20%, 40%, 60%, 80%, and 100%). A synthetic solution containing 50 mg of P/L (as KH_2PO_4) was supplied continuously at a rate of approximately 300 mL/day/column (equivalent to a nominal retention time in the columns of 4 h) using a constant-head feeding tank. The water level in the feeding tank was kept constant by continuously stirred storage tank kept at ground level. Water in the storage tank was renewed every first day. The columns were kept water saturated, as the effluent levels of the columns were set just above the surface of the filter medium C with oyster shell. The effluence and the volume of each column were measured daily to estimate actual loading. Samples of the influent and effluent were taken every first day and analyzed for P concentration for a period of 4 week in columns, using the molybdenum blue-ascorbic acid method (APHA, 1995).

Sequential chemical fractionation for inorganic P in the dry filter medium C with oyster shell samples was as follows: extraction with H_2O (water soluble-p, W–P), 25 g/L acetic acid and 1 mol/L NH_4Cl (calcium bounded P, Ca–P), 1 mol/L NH_4F (aluminum bounded P, Al–P), and 0.1 mol/L NaOH (iron bounded P, Fe–P). The amount of organic P (org-P) was estimated by the difference in the content after extraction with 0.5 mol/L H_2SO_4 before and after igniting the filter media sample at 350 °C for 1 h. The differences between the amount of total-P (digested with conc. $HClO_4$) and that of extracted inorganic P or organic P (inorg-P + org-P) was considered to correspond to residual insoluble P (Res-P) (Hirata et al., 1999).

2.5. Adsorption velocity of phosphorus

In order to obtain the adsorption velocity of the phosphorus depending on the oyster shell content in the filter medium C, which had the highest P adsorption capacity among the filter media can be used in the constructed wetland system, every effluent water for the HRT 0, 0.88, 1.76, 2.64 and 3.52 h was examined after 1 and 30 days of the column experiments. The P adsorption velocity of the oyster shell per level was examined using the linear equation $\ln(C/C_o) = -kt$ based on the phosphorus concentration in the influent and effluent water.

Adsorption velocity of phosphorus was applied by the linear velocity equation. Linear velocity can be expressed by $V = kC$. The reaction is related with a phosphorus concentration, the momentary reaction velocity of the time which C is changed as the dc can express in the dt by $-\mathrm{d}c/\mathrm{d}t$. Therefore, the Linear velocity Eq. (1) can express $-\mathrm{d}t/\mathrm{d}c$ at V in $V = kC$ if it substitutes.

Linear velocity Eq. (2) was induced as did the integral calculus linear velocity Eq. (1).

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = kC, \quad (3)$$

$$\ln \frac{C}{Co} = -kt, \quad (4)$$

where C is the concentration of phosphorus in solution at effluent (mg/L), Co is the concentration of phosphorus in solution at raw water (mg/L) and k is the P adsorption velocity constant, t is HRT (h).

3. Results and discussion

3.1. Batch experiments

3.1.1. Phosphorus adsorption capacity of the filter medium, the organic matter and the oyster shell

Langmuir isotherm experiments are applied in order to examine the maximum P adsorption capacity of the filter medium, the organic matter, and the oyster shell. As shown in Figs. 1 and 2 and Table 3, Langmuir isotherm plots show the positive (+) correlation with high significance for all tested filter media (for every grain size), the organic matter, and the oyster shell. The maximum P adsorption capacity for the grain size of the filter medium is: filter medium A (grain size: 4–10 mm) is 7.7 mg/kg; filter medium B (grain size: 2–4 mm) is 11.6 mg/kg; filter medium C (grain size: 0.1–2 mm) is 22.5 mg/kg, so the maximum P adsorption capacity increases as the grain size of the filter medium decreases. It is considered that the surface area to adsorb phosphorus increases as the grain size of the filter medium decreases. Also, the maximum P adsorption capacity of the oyster shell and the organic matter is examined to see the availability as an adsorbent: it is 833.3 mg/kg for the oyster shell, and 1001.1 mg/kg for the organic matter showing very superior P adsorption capacity. Accordingly, it is observed that the P adsorption capacity can be improved if these are used as an adsorbent, which is added in the filter medium.

If the oyster shell is used in the constructed wetland system with the design criteria (Area: 5 m^2; Depth: 0.6 m and Area: 10 m^2; Depth: 0.9 m) (Zhu et al., 1997), the phosphorus saturation is 0.83 g/kg and the longevity is 8–23 years. Comparing with shale (phosphorus saturation: 0.73 g/kg, longevity: 7–20 years) and EAF (phosphorus saturation: 1.35 g/kg, longevity: 13–37 years) (Drizo et al., 2002), we can obtain similar results.

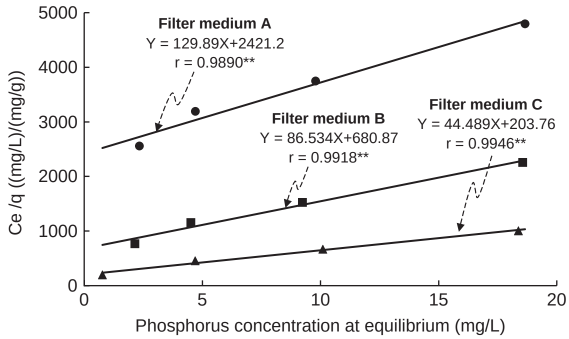

Fig. 1. Langmuir isotherm plot of the low initial phosphorus concentration in the incubation solutions (up to 20 mg/L) of the filter medium A, B, and C. The inverse of the slopes the regression lines were used to calculate maximum apparent P adsorption capacity. (* and ** denote significance at 5.0% and 1.0% levels, respectively).

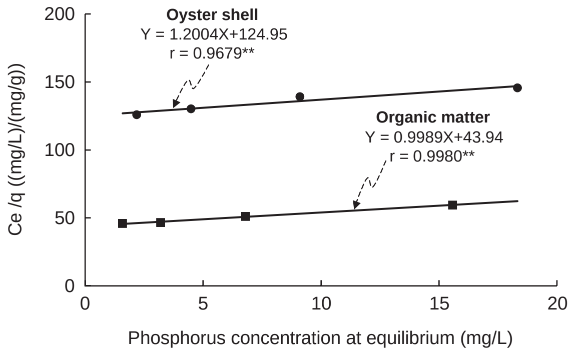

Fig. 2. Langmuir isotherm plot of the low initial phosphorus concentration in the incubation solutions (up to 20 mg/L) of the oyster shell, and organic matter. The inverse of the slopes the regression lines were used to calculate maximum apparent P adsorption capacity. (* and ** denote significance at 5.0% and 1.0% levels, respectively).

Table 3
Maximum P adsorption capacity (b), binding energy constants (a) and correlation coefficients (r) as estimated by Langmuir isotherm plot of filter media, oyster shell and organic matter

Materials	Langmuir isotherm P-adsorption capacity (b), (mg/kg)	P-bonding constant (a)	Correlation coefficients (r)
Filter medium A	7.7	5.36×10^{-5}	0.9890**
Filter medium B	11.6	1.27×10^{-4}	0.9918**
Filter medium C	22.5	2.18×10^{-4}	0.9946**
Oyster shell	833.3	9.60×10^{-6}	0.9679**
Organic matter	1001.1	2.27×10^{-5}	0.9980**

(* and ** denote significance at 5.0% and 1.0% levels, respectively).

3.1.2. Phosphorus adsorption capacity of filter media when supplemented with organic matter

Organic matters are accumulated by the sewage, which is flowed in the constructed wetland every elapsed time of the sewage treatment, and by the naturalized perennial water plants. Most organic matters included in the sewage are soluble, thus microbes can be used as the energy source; however, it takes much time for the withered and dead water plants accumulated in the constructed wetland to be corroded completely. Therefore, in order to examine how the P adsorption capacity is affected by the organic matters caused by water plants among those organic matters accumulated in the constructed wetland, we mixed evenly the perennial water plants (i.e., *P. communis* T_{RIN}, *P. japonica* S_{TEUD}, *C. dispalata* B_{OOTT}, *I. pseudoacorus* L.), accumulated and corroded in the constructed wetland to prepare the organic matters. Then, we added 0%, 3%, and 5% organic matters to the filter medium, and examined the P adsorption capacity. The maximum P adsorption capacity was applied to Langmuir isotherm experiment depending on the addition of organic matters per grain size of the filter medium. The result is shown in Fig. 3. When 0%, 3%, and 5% organic matters were added per grain size of the filter medium, the maximum P adsorption capacities were increased more and more for all filter media, and in particular, the addition of 5% organic matter to the filter medium C has rapidly increased P adsorption capacity comparing with those without the organic matters: namely, the P adsorption capacity was increased to 76 mg/kg, by 53 mg/kg. Likewise, the maximum P adsorption capacity is increased by adding the organic matter because it is considered that the organic matter itself gives very high P adsorption capacity as shown in the previous experiments of the maximum P adsorption capacity of the filter medium (for every grain size), the organic matter, and the oyster shell. However, one of the characteristics of the organic matter is the very high phosphorus content, so the phosphorus may be rather released if the organic matter is injected more than a limit. With this, it is determined that it should not be injected more than the amount naturally accumulated by water plants in the constructed wetland. Therefore, it is considered that the organic matter made of the accumulated and corroded water plants in the constructed wetland can increase the P adsorption capacity, accordingly improving the P adsorption capacity.

3.1.3. Phosphorus adsorption capacity of filter medium C when supplemented with Ca, Mg, Al, Fe and oyster shell

We added Ca, Al and Fe, which can be injected with the sewage, to the filter medium with filter medium C having the highest P adsorption capacity, in order to see how Ca, Al and Fe affect the P adsorption capacity. Also, when we added the oyster shell (Choi and Wang, 1999) which is a waste and has high Ca content to recycle it, we examined how it affected to the P adsorption. Because pH affects largely the P adsorption and precipitation when Ca, Al, Fe and the oyster shell are added to the filter medium C, the P adsorption capacity experiment was performed in pH 6–8, which is the same condition as that of the general domestic sewage. The result is shown in Fig. 4. When Ca, Mg, Al and Fe were added to the filter medium C, the maximum P adsorption capacity of the filter medium C was generally increased as every addition increased. Especially, in case of Ca addition, only 0.1% Ca, which is

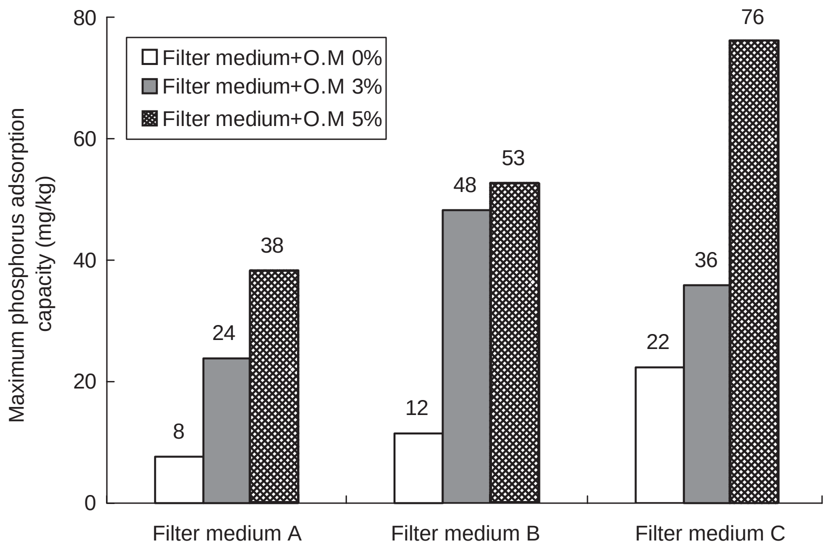

Fig. 3. Maximum P adsorption capacity of filter media supplemented with different level of organic matters.

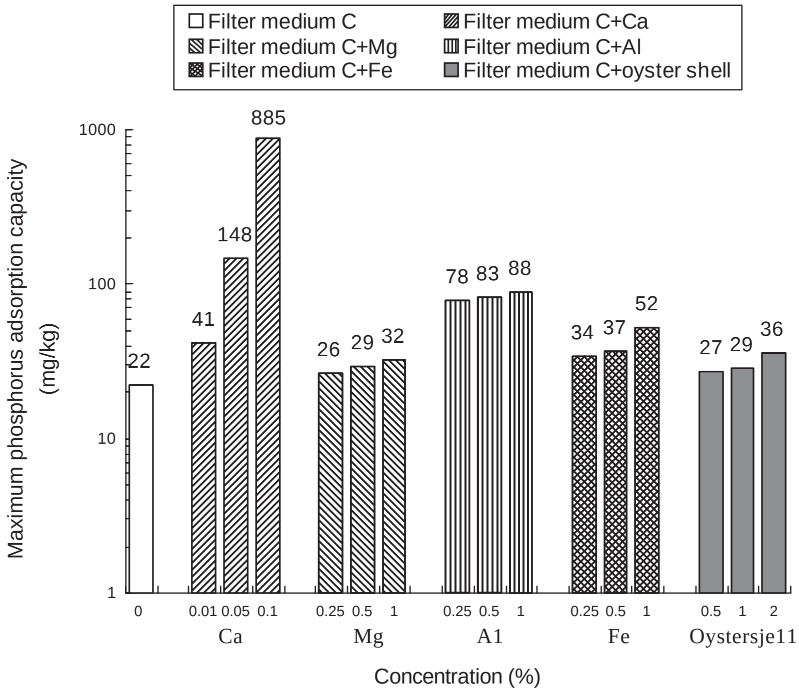

Fig. 4. Maximum P adsorption capacity of filter media C when supplemented with Ca, Mg, Al, Fe and oyster shell.

relatively small amount comparing with other additions, can rapidly increase the P adsorption capacity up to 885 mg/kg. However, although the P adsorption is increased with high significance by the addition of Ca, Mg, Al and Fe to the constructed wetland, they may induce the secondary pollution, so it is determined that they are not allowed to be injected to the sewage treatment plant. Therefore, we examined the P adsorption capacity after adding the oyster shell, which does not induce the secondary pollution because of its low solubility after adsorbing the phosphorus and can increase the P adsorption capacity rapidly with small quantity because of its high Ca content. As a result, when 0.5%, 1% and 2% oyster shell were added, the P adsorption capacity was constantly increased to 27, 29 and 36 mg/kg, respectively. Addition of 2% oyster shell gave 13 mg/kg increase of P adsorption capacity comparing with those without addition. Therefore, if filter medium C and oyster shell are mixed to be used as the filter medium for the construction of the constructed wetland, the secondary pollution will not be induced while improving the accumulating capacity of phosphorus, so it is considered that the longevity of the constructed wetland can be extended.

3.2. Column experiments

3.2.1. Phosphorus saturation for filter media C when supplemented with oyster shell

Among the filter medium that can be used in the constructed wetland, we injected the oyster shell per level to the filter medium C, which has the highest adsorption capacity, through batch experiment, in order to improve the P adsorption capacity. Fig. 5 shows the corresponding phosphorus concentration changes. 100 g of mixed filter medium where 0%, 5%, 10%, 20%, 40%, 60%, 80%, and 100% content of oyster shell were injected into the filter medium C was repeated three times, and 50 mg/L of standard phosphorus solution (KH_2PO_4) was injected continuously for a month at 300 mL/day (HRT 3.52 h). After examining the phosphorus concentration change in every column, in case that the oyster shell content was 0% in the filter medium C, about 32.0 mg/L was flowed out at first, and then the effluent phosphorus concentration approached 50 mg/L, the influent phosphorus concentration, due to the decrease of the P adsorption capacity as the treatment time went by. Finally, the saturation state was reached where almost no adsorption occurred about 4 days later. Besides, in case that the oyster shell content was 5%, 10%, 20%, and 40% in the filter medium C, about 29.0, 25.1, 18.8, and 17.0 mg/L were flowed out at first, respectively, and then every saturation state, where no adsorption occurred, was reached about 6, 9, 17, and 30 days later. However, in case that the oyster shell content was 60%, 80%, and 100% in the filter medium C, the respective effluent concentrations were 11.1, 8.33, and 5.87 mg/L, adsorbing phosphorus constantly and stably. Therefore, although we could not examine all saturation states within a month, if we express the saturation time for 5%, 10%, 20%, and 40% oyster shell content

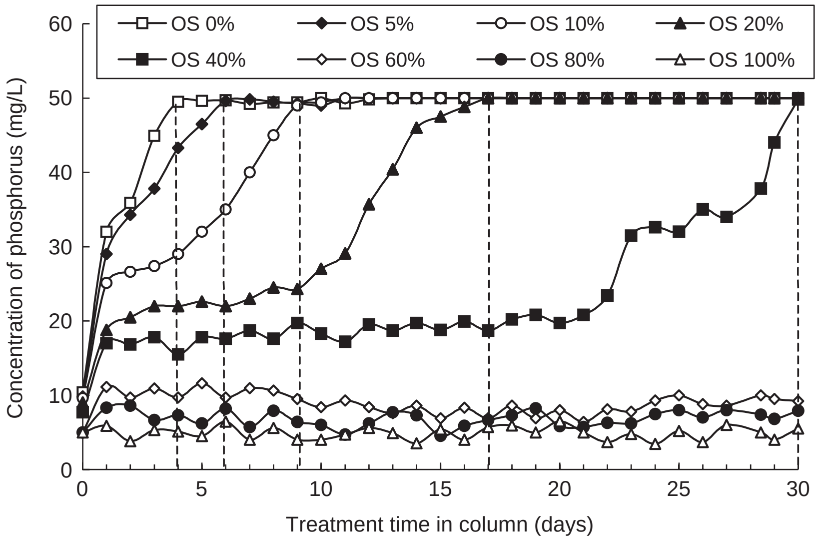

Fig. 5. Variation of phosphorus in effluent according to filter media mixed with oyster shell (OS) in column.

as the linear regression equation, it is $Y = 0.6629X + 3.2(r = 0.9903^{**})$, from which we can predict the saturation time of the phosphorus for 60%, 80%, and 100%. The respective predicted saturation times for 60%, 80%, and 100% oyster shell content are about 43, 56, and 70 days. Based on this, it is considered that the longevity of the constructed wetland system by the phosphorus saturation can be extended by adding the oyster shell. Consequently, if the filter medium C is used for the currently operating constructed wetland sewage treatment plant (inflow: 15 m^3/day; phosphorus concentration: 6 mg/L; area: 75 m^2; depth: 1 m), the phosphorus saturation time is predicted about 3–5 years, but it is considered that the longevity of the sewage treatment plant can be extended up to 10–12 years by adding about 20% oyster shell to the filter medium C.

Therefore, it is determined that the adsorption amount of phosphorus can be increased by injecting the oyster shell, and that the longevity of the constructed wetland can be extended due to the phosphorus saturation by adding the oyster shell to the filter medium C in the constructed wetland. Furthermore, it is considered that using the oyster shell can be a scheme to reduce the environmental pollution in aspect of recycling waste.

The P adsorption amount was examined considering the phosphorus concentration drained for 1 month in the column experiment. Fig. 6 shows the result. In case that the oyster shell content was 0% in the filter medium C, the P adsorption amount was about 180 mg/kg for 1 month. As the oyster shell increased, the P adsorption amount increased gradually. When the oyster shell content was 5%, 10%, 20%, 40%, 60%, 80% and 100%, the P adsorption amount for 1 month was about 600, 1560, 4280, 6157, 7089, 7519, and 7925 mg/kg, respectively, and the increment of the P adsorption amount was small if the oyster shell content was 60% or more because the filter medium with more than 60% oyster shell content did not approach the saturation time by the P adsorption yet. If the P adsorption amount for 5%, 10%, 20%, and 40% oyster shell content is expressed as the linear regression equation, it is $Y = 158.83X + 173.03(r = 0.9774^{**})$. Based on this equation, the P adsorption amount for 60%, 80% and 100% can be predicted as about 9702, 12,879, and 16,056 mg/kg, respectively.

3.2.2. *Adsorption velocity of the phosphorus*

In order to obtain the adsorption velocity of the phosphorus depending on the oyster shell content in the filter medium C, which had the highest P adsorption capacity among the filter medium can be used in the constructed wetland system, every effluent water for the HRT 0, 0.88, 1.76, 2.64, and 3.52 h was examined after 1 and 30 days of the column experiment. All P adsorption velocity equations have negative correlation with high significance. The P adsorption velocity of the oyster shell per level was examined using the linear equation $\ln(C/C_o) = -kt$ based on the phosphorus concentration in the influent water and the effluent water. Fig. 7 and Table 4 show the result. For the P adsorption velocity after 1 day of the column experiment, when the oyster shell content was 0%, 5%, 10%, 20%, 40%, 60%, 80%, and 100%, the respective P adsorption velocity constant (K) were 3.18, 3.89, 4.92, 6.98, 7.71, 10.75, 12.80, and 15.30/h, so it increases gradually as the oyster shell content increases. After 30 days of the column experiment, each P adsorption velocity constant

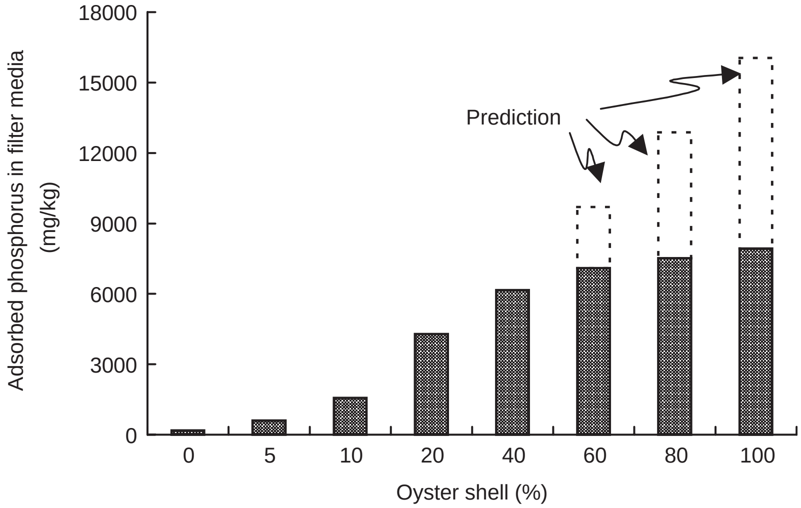

Fig. 6. Adsorbed phosphorus in filter media according to treatment amount of oyster shells in column.

(K) of the P adsorption velocity for the oyster shell content 0%, 5%, 10%, 20%, 40%, 60%, 80%, and 100% was 0.028, 0.014, 0.028, 0.028, 1.06, 12.09, 13.17, and 15.76/h, respectively. The P adsorption velocity constant for 0%, 5%, 10%, and 20% oyster shell content after 30 days of the column experiment was closer to 0.02/h than 1 day, so the P adsorption was saturated. In case of 40% oyster shell content, the P adsorption velocity decreased more rapidly after 30 days than after 1 day, consequently assuming that the phosphorus in the filter medium was gradually saturated. However, 60%, 80%, and 100% oyster shell content showed little differences in the P adsorption velocity both after 1 and 30 days of the column experiment, so we can assumed that the P adsorption capacity of the filter medium was already improved by adding the oyster shell so that the saturation time was delayed. Therefore, the HRT and the phosphorus concentration in the column can be predicted from the P adsorption velocity constant per filter medium, and it is important as a basic result in order to remove the P adsorption in the constructed wetland system. Especially, it will be a very vital factor to determine the depth and the HRT of the filter medium at the time of designing the constructed wetland system.

3.2.3. *Phosphorus fractionation*

We performed the column experiment of the phosphorus after 30 days depending on the oyster shell content in the filter medium C, which is the highest P adsorption capacity among those filter media, can be used in the constructed wetland system. Table 5 shows the P fractionation result of the phosphorus among the filter medium. Total P content was about 136.9 mg/kg

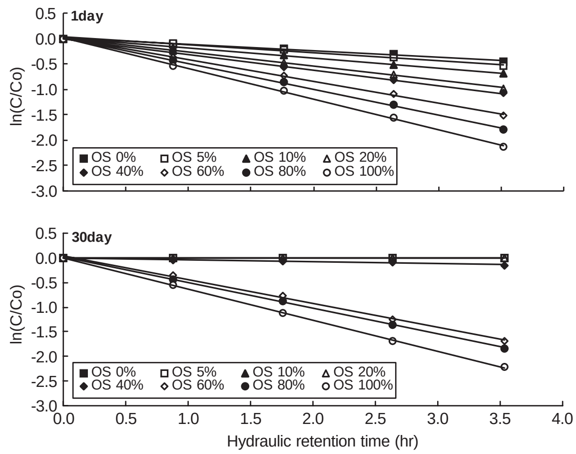

Fig. 7. Adsorption velocity of phosphorus in the filter media mixed with oyster shell (OS) according to the hydraulic retention time at 1 and 30 days after phosphorus solution treatment in column.

for 0% oyster shell and 932.8 mg/kg for 100% oyster shell content, so the total P content to the filter medium gradually increased as the oyster shell content increased. It is considered that organic P content is not increased by the injected phosphorus solution, but is the content from the filter medium and the oyster shell themselves.

Inorganic and residual P increase rapidly as the content of the oyster shell increases, so most total P can be considered as inorganic and residual P. Extractable P was about 9.40 mg/kg for 0% oyster shell and 95.33 mg/kg for 100% oyster shell, thus extractable P content for

Table 4
Linear equation, P adsorption velocity constant and correlation coefficients (r) of filter media mixed with oyster shells according to the hydraulic retention time at 1 and 30 days after phosphorus solution treatment in column

Treatment time	Materials (%)	Linear equation	Adsorption velocity constant (K)	Correlation coefficients (r)
1day	Oyster shell 0	$Y = -0.1242X + 0.0073$	3.18	0.992**
	Oyster shell 5	$Y = -0.1545X + 0.0229$	3.89	0.990**
	Oyster shell 10	$Y = -0.1950X + 0.0038$	4.92	0.999**
	Oyster shell 20	$Y = -0.2748X + 0.0028$	6.98	0.999**
	Oyster shell 40	$Y = -0.3054X - 0.0118$	7.71	0.999**
	Oyster shell 60	$Y = -0.4242X + 0.0050$	10.75	0.999**
	Oyster shell 80	$Y = -0.5057X + 0.0164$	12.80	0.999**
	Oyster shell 100	$Y = -0.6040X + 0.0124$	15.30	0.999**
30day	Oyster shell 0	$Y = -0.0052X - 0.0036$	0.028	0.823*
	Oyster shell 5	$Y = -0.0078X - 0.0024$	0.014	0.960**
	Oyster shell 10	$Y = -0.0065X - 0.0044$	0.028	0.847*
	Oyster shell 20	$Y = -0.0027X + 0.0008$	0.028	0.953**
	Oyster shell 40	$Y = -0.0409X + 0.0016$	1.060	0.993**
	Oyster shell 60	$Y = -0.4861X + 0.0455$	12.09	0.997**
	Oyster shell 80	$Y = -0.5242X + 0.0241$	13.17	0.999**
	Oyster shell 100	$Y = -0.6317X - 0.0013$	15.76	0.999**

(* and ** denote significance at 5.0% and 1.0% levels, respectively).

Table 5
P fractionation of phosphorus in the filter media mixed with oyster shell after 30 days of P solution application

Items	Oyster shells (%)							
	0	5	10	20	40 (mg/kg)	60	80	100
Total-P	136.90	158.40	281.20	313.00	513.10	563.20	646.10	932.80
Organic-P	0.30	0.60	1.20	2.40	4.80	7.40	9.50	12.20
Inorganic-P	53.54	63.70	63.72	104.79	189.10	182.95	271.11	380.95
Residual-P	78.70	94.90	217.30	212.50	316.20	378.00	364.20	522.30
Extractable-P	9.40	18.92	30.58	50.19	57.04	66.39	82.04	95.33
Water soluble-P	1.64	2.15	2.19	2.09	1.13	1.26	1.36	0.78
Ca–P	6.67	15.99	27.88	47.66	55.58	65.00	80.55	94.47
Al–P	1.07	0.76	0.49	0.41	0.29	0.11	0.10	0.03
Fe–P	0.02	0.02	0.02	0.03	0.04	0.02	0.03	0.05

the filter medium increases rapidly as the content of the oyster shell increases.

The results revealed that the largest amount of extracted P in filter media with oyster shell after 30 days of P solution application was bound to Ca, followed by water soluble-P, Al–P, Fe–P because it is assumed that the oyster shell has 34% Ca (94% CaO) and most extractable P is bound to Ca of the oyster shell. Therefore, it is considered that the P adsorption capacity is improved by the oyster shell, which is selected as the waste to inject Ca, which is efficient to improve the P adsorption capacity more than Al and Fe, into the constructed wetland, consequently available to extend the longevity of the constructed wetland.

4. Conclusion

In this study, the phosphorus adsorption capacities of various filter media were investigated in relation to the size and types of filter media to screen the optimal condition. The P adsorption capacity was examined per grain size of sand to select the optimum filter medium. The maximum P adsorption capacities of filter media A

(4–10 mm), B (2–4 mm), and C (0.1–2 mm) were 7.7, 11.6, and 22.5 mg/kg, respectively, showing those increased as the filter media size decreased. Among our experimental media, the optimal filter media size was 0.1–2 mm. When Ca, Mg, Al and Fe were added to the filter medium C, Ca improved mostly the P adsorption capacity.

In the column where the oyster shell was mixed, when 10%, 40% and 100% of oyster shell content was added to the filter medium C, the saturation time of the P adsorption was about 9, 30 and 70 days, respectively. Therefore, we can assume that the P adsorption capacity of the filter medium was improved by adding the oyster shell. The largest amount of extracted P in filter media with oyster shell after 30 days of P solution application was Ca–P form, followed by water soluble-P, Al–P, Fe–P.

Therefore, it was concluded that the adsorption amount of the phosphorus could be increased by adding the oyster shell to the filter medium. It was also concluded that adding the oyster shell to the filter medium in the constructed wetland was the scheme to extend the longevity of the constructed wetland by the P saturation, and using the oyster shell would be useful in aspect of economical efficiency and easiness. Especially, it would be the alternative proposal to reduce the environmental pollution in aspect of recycling wastes.

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