

Original Research

Phosphorus Adsorption Capacity Evaluation for the Substrates Used in Constructed Wetland Systems: a Comparative Study

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Abstract

To provide a selection criteria to choose substrates according to the quality of the water requiring treatment in constructed wetlands (CWs), phosphorus (P) adsorption properties of four quartz sands with different physicochemical characteristics and four substrates commonly used in CWs were tested and evaluated via both the Langmuir and Freundlich equations. The effects of organic matters (OM) on P adsorption capacities of the substrates were also studied to evaluate the practical values of the substrates. The Langmuir sorption isotherm was used to estimate the P adsorption capacities of the tested substrates in CWs. Overall, the maximum P adsorption for all of the tested substrates decreased as follows: furnace slag > ceramic > zeolite > activated carbon > quartz quartz sands. The P adsorption capacities were significantly influenced by grain size; specific surface area; Fe, Al, Mg, and Ca contents in the substrates; and the amount of added OM. The chemical precipitation of P by the substrates containing Fe was more effective than those containing Ca at the same level. Added OM impacts P sorption by influencing pH, and substrates containing higher Fe and Al concentrations and lower Ca concentrations were more resistant to decreases in the P adsorption capacities due to OM accumulation. Finally, a principle for selecting substrates for the treatment of wastewater with different characteristics was determined.

Keywords: Phosphorus adsorption, substrates, Langmuir adsorption isotherm, Freundlich adsorption isotherm, organic matters (OM)

Introduction

CWs have been designed and constructed to use natural processes for the removal of pollutants from contaminated water in a more controlled environment [1-3]. Previous results have shown that substrate adsorption plays the most important role in P immobilization [4-8]. Therefore, cheap and effective P adsorbents are highly desirable [9-11].

The most commonly used substrates in CWs are quartz sands [12], activated carbon (AC) [12-13], zeolite [14], ceramic [15], and furnace slag [16-17], and prior research has shown that the removal of P by these substrates mainly occurs through physical adsorption, chemical precipitation, and ion exchange [10-11]. However, P sorption properties of the substrates have not been systematically estimated, which resulted in many defective packing layer designs for CWs [3, 11]. Thus, it is important to evaluate the P adsorption properties of the substrates before full-scale use was performed.

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The Langmuir isotherm is a physical adsorption model that was calculated on the basis of assuming the adsorbed gas form monomolecular layer on a uniform surface [18–19]. The greatest advantage of the application of Langmuir in adsorption study is that it enables the estimate of the theoretical P adsorption maximum of a substrate [9, 20]. The Freundlich equation was also developed to evaluate adsorption performance. Unlike the Langmuir equation, the Freundlich equation is a physical-chemical adsorption model developed based on both physical adsorption and chemical adsorption via reaction or iron exchange [18, 20]. Thus, the P sorption capacity of substrates should be evaluated using both the Langmuir and the Freundlich equations.

The functions of CWs for treating wastewater largely depend on the accumulation, cycling, and decomposition of OM, and OM accumulation is a typical feature of CWs [3, 10]. However, the accumulation of OM could potentially contribute to the pore clogging of the substrates [10], which reduces the substrate-flow in CWs and may decrease the hydraulic retention time (HRT) and P and N removal efficiency. Therefore, it is also important to experimentally investigate the impacts of OM on P sorption to evaluate the practical values of the substrates.

To provide a selection criteria that can be used to choose substrates according to the quality of the water requiring treatment in CWs, P sorption properties of four quartz sands with different physicochemical characteristics and four other substrates commonly used in CWs were tested and evaluated using both the Langmuir and the Freundlich equations in the present study. The effects of OM on the P sorption capacities of the substrates were also studied to evaluate the practical values of the substrates.

Materials and Methods

The Tested Substrates

Eight substrates that are frequently applied in CWs were chosen: four types of quartz sands, furnace slag, zeolite, ceramic, and AC. The four types of quartz sands were chosen for the present study to investigate the impacts of particle size and the chemical characteristics of substrates on P adsorption (I and II had nearly the same particle size distribution and different chemical characteristics; II and III had nearly the same chemical characteristics and different particle size distributions; and I and IV had nearly the same particle size distribution and chemical characteristics with different Fe and Ca contents, although the total Fe and Ca contents were nearly equal). The furnace slag used in this study was produced by steel mills. Furnace slag, zeolite, ceramic, and AC have been commonly used to enhance the contaminant removal capabilities of CWs. Elemental distribution, pH, and particle size distribution of the substrates are shown in Tables 1 and 2.

Table 1. Chemical characteristics of the substrates.

Materials	Fe (g kg ⁻¹)	Ca (g kg ⁻¹)	Al (g kg ⁻¹)	Mg (g kg ⁻¹)	pH
Quartz sand I	3.34	56.4	1.34	1.26	7.38
Quartz sand II	2.27	35.4	1.51	1.12	7.08
Quartz sand III	2.65	37.6	1.45	1.39	7.19
Quartz sand IV	12.31	47.3	1.37	1.65	7.61
AC	—	—	—	—	6.95
Zeolite	15.1	12.3	71.6	3.14	10.4
Ceramic	1.32	22.7	82.8	1.39	9.84
Furnace slag	19.4	15.66	38.8	0.41	12.1

Table 2. Grain size distribution of each candidate substrate (mass fraction/%).

Substrates	0.0-0.5 mm	0.5-1.0 mm	1.0-2.0 mm	2.0-5.0 mm
Quartz sand I	19.1	47.7	22.8	10.4
Quartz sand II	19.6	50.1	18.7	11.6
Quartz sand III	13.9	15.0	27.7	43.4
Quartz sand IV	18.5	46.3	22.7	12.5
AC	0.0	0.0	67.1	32.9
Zeolite	0.0	0.9	58.1	41.0
Ceramic	0.0	1.5	43.0	55.5
Furnace slag	5.9	7.9	34.3	61.9

P Adsorption Experiment for the Substrates

Equilibrium adsorption experiments were conducted for all of the chosen substrates. 4 g of each dried (at 105°C for 2 h) substrate was settled into 100 mL centrifuge tubes containing 80 mL NaCl solution (0.05 mol L⁻¹) prepared in deionized water with NaH₂PO₄ (pH 7.0±0.1) at P concentrations of 50, 100, 200, 300, 400, 600, 800, and 1,000 mg L⁻¹ for the ceramic, zeolite AC and furnace slag, and AC, and 5, 10, 20, 30, 40, 60, 80, and 100 mg L⁻¹ for the quartz sands. The centrifuge tubes without substrate were used as a blank control group, and 0.5 mL of chloroform was added to all the tubes as bacterial inhibitor. The tubes were sealed and shaken using a constant temperature shaker for 24 h (165 rpm, 25°C), and samples were taken and centrifuged for 15 min at 4,500 rpm. Then the supernatant solutions were filtered through 0.45 µm filters, and the P concentrations were determined, and the P concentrations in the supernatant solutions were determined. Three parallel measurements

were performed for each sample, and the mean and limits of error were also determined. The Langmuir and Freundlich equations were simultaneously used to determine the relationship between the P adsorption capacity of the substrates and the P concentration in the equilibrium solutions. The Langmuir equation is defined as follows:

$$q = ab\rho_e / (1+b\rho_e) \quad (1)$$

...and the Freundlich equation can be written as

$$q = k\rho_e^{1/n} \quad (2)$$

...where q is amount of adsorbed P (mg g^{-1}), ρ_e is the concentration of P in the solution at equilibrium (mg L^{-1}), a is the apparent P adsorption capacity (mg g^{-1}), b is a constant related to the binding strength of P, and k is the apparent sorption rate constant. All data processing was conducted using DPS software [21].

Impacts of OM on P Sorption

Peat purchased from the local plant market had TC content of $499.7 \pm 9.1 \text{ g kg}^{-1}$, and pH of 5.93 ± 0.20 was used as OM. The relative influences of OM on the sorption capacities of the substrates were investigated by mixing peat with the furnace slag, ceramic, zeolite, and AC because they are commonly used to enhance the process capacity of CWs. Five peat amendment levels were used (0%, 4%, 8%, 12%, and 16% of total weight of the mixtures), with triplicate samples for each level. First, the mixtures were dried at 105°C for 2 h, then 5 g of each mixture were placed in 250 mL Erlenmeyer glass flasks. A 500 mg kg^{-1} P solution was prepared in deionized water and amended with furnace slag, ceramic, zeolite, and AC. Then 1 mL of chloroform was added. The flasks were sealed and settled in a constant temperature shaker for 48 h (165 rpm, 25°C). Samples were taken and centrifuged, and aliquots of the supernatant solutions were filtered through $0.45 \mu\text{m}$ filters, and the P concentrations and pH of the filtered solutions were determined.

Analytical Methods

TC content of the peat was determined using a TOC analyzer [22], and the pH values of the substrates were detected by a pH meter in a 2.5:1 (volume ratio) water/substrate mixture after 24 hours' equilibration. P concentrations were measured by the molybdenum blue method with a total phosphorus analyzer, and P removed by the substrate was calculated as a decrease in the P concentration in the solutions. The experimental pH variations were determined using a pH probe. The Fe, Ca, Al, and Mg contents in the substrates were analyzed via an atomic absorption spectrophotometer after being extracted in boiling $\text{HNO}_3\text{-H}_2\text{O}_2$ [23].

Results and Discussion

P Adsorption Capacities of the Substrates

The relationships between the equilibrium P concentrations in solution and the amounts of P adsorbed for different substrates are shown in Fig. 1. The apparent P adsorption capacities of the substrates were estimated

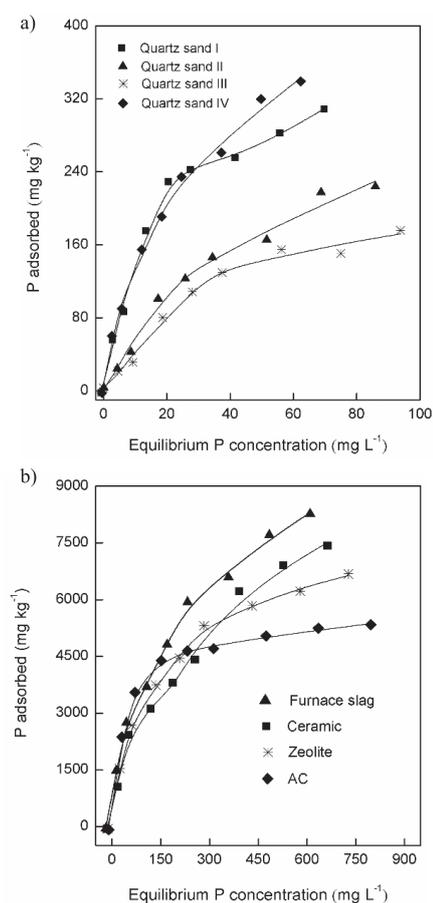


Fig. 1. Relationship between equilibrium a) P concentration and b) the P adsorbed.

Table 3. Langmuir sorption isotherm coefficients for the tested substrates.

Substrates	P sorption maximum (g kg^{-1})	Binding energy
Quartz sand I	0.30 ± 0.02	0.019 ± 0.001
Quartz sand II	0.21 ± 0.01	0.027 ± 0.002
Quartz sand III	0.18 ± 0.01	0.048 ± 0.002
Quartz sand IV	0.33 ± 0.03	0.035 ± 0.002
AC	4.64 ± 0.05	0.017 ± 0.001
Zeolite	6.78 ± 0.09	0.031 ± 0.002
Ceramic	7.24 ± 0.12	0.022 ± 0.001
Furnace slag	8.11 ± 0.10	0.024 ± 0.003

using the linear form of the Langmuir equation and is shown in Table 3. Preliminary experiments showed that the furnace slag, ceramic, zeolite, and AC adsorbed almost all of the P in the solution during a short period when P concentration was below 100 mg L^{-1} , which was not observed in the quartz sands treatments. Therefore, two series of P solutions were used. As shown in Fig. 1, the quantities of P adsorbed by the substrates were significantly varied when plotted as a function of the P concentration in the equilibrium solutions. The Langmuir adsorption maximums, as well as the binding energies, also varied significantly. The P adsorption maximums varied between $8.11 \pm 0.10 \text{ g kg}^{-1}$ for the slag and 0.18 ± 0.01 for quartz sand III (Table 3). The maximum P adsorptions of the four quartz sands increased as follows: quartz sand III < quartz sand II < quartz sand I < quartz sand IV. Overall, the maximum P sorption for all of the tested substrates increased as follows: quartz sands (III < II < I < IV) < activated carbon < zeolite < ceramic < furnace slag. The results of the present study demonstrated that the P adsorption capacities of substrates vary significantly; these findings are comparable with those reported in the literature [12, 24-26].

P adsorption capacity of quartz sand II was higher than quartz sand III (Fig. 1) because quartz sand II had a finer grain size (Table 1). The P adsorption capacities were impacted by the grain size of substrates because the substrates with fine grain sizes had larger specific surface areas, which can potentially enhance the P sorption capacity. Previous studies have also shown that Al/Fe-bound P is correlated significantly with a proportion of the fine fraction [27]. P sorption capacities were also impacted by the chemical characteristics of the substrates because P could be precipitated when reacted with ionic Fe, Ca, Al, or Mg [10, 28-29]. Studies by David [30] and Xu et al. [10] also showed that the P removal efficiency and sorption capacity are significantly affected by the Fe, Ca, Al, and Mg contents. In this study, the P adsorption capacities of the quartz sands (I, II-IV) were positively correlated with the Fe and Ca contents. The differences between quartz sand I and quartz sand IV regarding their P sorption capacity also indicated that the enhancement of Fe on P sorption was stronger than that of Ca at the same

concentrations (Fig. 1 and Table 1). Fe extraction using ammonium oxalate from solution was also found to be a good indicator of P adsorption via ionic Fe [31]. Thus, more dissolved Fe would result in more P precipitation and is related to higher total amounts of Fe in the substrates [32]. Furnace slag also resulted in a higher P sorption capacity than ceramic (Table 3) because of the higher Fe content (Table 1). When comparing the adsorption isotherms of AC, zeolite, and ceramic, the substrate with the highest specific surface area (AC) was quickly saturated and had a higher P sorption rate. However, the substrates with much lower specific surface areas and higher Fe, Ca, Al, and Mg contents become saturated slowly, although they eventually reached a higher P sorption capacity because releasing metallic ions and P precipitation were much slower than physical adsorption [28, 31]. As shown in Fig. 1 and Table 3, the furnace slag exhibited a relatively higher P adsorption capacity than the quartz sands, ceramic, zeolite, and AC, with a P sorption maximum of $8.11 \pm 0.10 \text{ g kg}^{-1}$.

Adsorption Isotherm

Based on the results of the P adsorption experiment, the Langmuir and Freundlich equations were simultaneously used to examine the relationship between P adsorption capacities of the substrates and P concentrations in the equilibrium solutions. The correlation coefficients (R^2) and other reaction constants are shown in Tables 4 and 5.

Tables 4 and 5 show that the Langmuir and Freundlich adsorption equations both provide a good relationship between the equilibrium P concentrations in solution and the amounts of P adsorbed for different substrates; the R^2 were 0.655-0.992. However, the R^2 of the substrates based on the same adsorption equation varied. For example, the R^2 of quartz sand II, AC, and zeolite based on the *Langmuir* adsorption equation were 0.911-0.992, whereas for quartz sands I and III-IV, ceramic, and furnace slag, the values were 0.811-0.876. The R^2 calculated for the Langmuir adsorption equation decreased as follows: AC > zeolite > quartz sand II > quartz sand III > quartz sand I > ceramic > furnace slag > quartz sand IV. The R^2 for the same substrates but with different adsorption

Table 4. P adsorption model and related parameters of the substrates based on the Langmuir equation.

Substrates	Langmuir adsorption isotherm	Correlation coefficient (R^2)	$a/(\text{g kg}^{-1})$	b
Quartz sand I	$q = 0.00570\rho_e/(1+0.019\rho_e)$	0.828	0.30	0.019
Quartz sand II	$q = 0.00567\rho_e/(1+0.027\rho_e)$	0.911	0.21	0.027
Quartz sand III	$q = 0.00864\rho_e/(1+0.048\rho_e)$	0.876	0.18	0.048
Quartz sand IV	$q = 0.01155\rho_e/(1+0.035\rho_e)$	0.811	0.33	0.035
AC	$q = 0.07881\rho_e/(1+0.017\rho_e)$	0.992	4.64	0.017
Zeolite	$q = 0.2105\rho_e/(1+0.031\rho_e)$	0.901	6.78	0.031
Ceramic	$q = 0.1590\rho_e/(1+0.022\rho_e)$	0.816	7.24	0.022
Furnace slag	$q = 0.1955\rho_e/(1+0.024\rho_e)$	0.815	8.11	0.024

Table 5. P adsorption model and related parameters of the substrates based on the Freundlich equation.

Substrates	Freundlich adsorption isotherm	R^2	n
Quartz sand I	$q = 0.0107 \rho_e^{0.730}$	0.833	1.37
Quartz sand II	$q = 0.0197 \rho_e^{0.535}$	0.797	1.87
Quartz sand III	$q = 0.0225 \rho_e^{0.439}$	0.831	2.28
Quartz sand IV	$q = 0.0310 \rho_e^{0.602}$	0.874	1.66
AC	$q = 0.0660 \rho_e^{0.402}$	0.655	2.49
Zeolite	$q = 0.0324 \rho_e^{0.469}$	0.839	2.13
Ceramic	$q = 0.0655 \rho_e^{0.465}$	0.830	2.15
Furnace slag	$q = 0.0451 \rho_e^{0.676}$	0.907	1.48

equations were also different. For example, for AC and furnace slag the R^2 calculated via the Langmuir adsorption equation were 0.992 and 0.815, respectively, whereas the values were 0.655 and 0.907 when calculated based on the Freundlich adsorption equation. The R^2 calculated using the Freundlich adsorption equation decreased as follows: furnace slag > quartz sand IV > quartz sand I > zeolite > quartz sand III > ceramic > quartz sand II > AC.

The Langmuir isotherm is a physical adsorption model that was calculated on the basis of assuming that the adsorbed gas forms the monomolecular layer on a uniform surface [18-19], which indicates that the P adsorption isotherm of the substrates with finer grain sizes or higher specific surface areas could be more properly fitted by the Langmuir than the Freundlich equation. Thus, the R^2 of quartz sand II was higher than that of quartz sand III when fitted using Langmuir due to its finer grain size, and the R^2 for AC was the highest among the tested substrates because it had the highest specific surface area (Table 1). Furthermore, the Freundlich equation is a physical-chemical adsorption model developed based on both physical adsorption and chemical adsorption by reaction or iron exchange [18, 20]; thus, the P adsorption isotherm of the substrates with higher Fe, Ca, Al, and Mg contents could be better fitted by the Freundlich equation. As a result, the R^2 value of quartz sand I when fitted with the Freundlich equation was higher than that of quartz sand II due to its higher Ca content, and AC had a lower R^2 value than zeolite, ceramic, and furnace slag due to the absence of Fe, Ca, Al, and Mg (Table 2). Comparing the chemical composition and the R^2 of quartz sand I and IV, it was found that they had nearly equal Fe and Ca content sums, although quartz sand IV had a higher Fe content and lower Fe content than quartz sand I (the Fe and Ca contents of quartz sand I were 3.36 g kg⁻¹ and 56.4 g kg⁻¹, while that for quartz sand IV were 12.31g kg⁻¹ and 47.4 g kg⁻¹). Tables 4 and 5 show that the R^2 value of quartz sand IV was higher and lower than that of quartz sand I when fitted using the Freundlich and Langmuir equations, respectively, indicating that the chemical precipitation of P by the substrates containing Fe

was more effective than those containing Ca at the same content. This finding also explains the difference in R^2 between ceramic and zeolite when fitted by the different adsorption equations.

Effects of OM on P Adsorption Capacities of the Substrates

In all the treatments, adding OM (peat) decreased the pH of the solutions because the pH of OM is 5.93±0.20. The pH increased with time and then remained steady (Fig. 2). The pH of the AC remained steady only after 4 h, and the pH of the other substrates remained steady after 8 h. For example, when the amount of OM rose (0% to 16%), pH in the solution in slag treatment decreased (12.23 to 8.86), and pH of the solutions in ceramic and zeolite treatment decreased from 9.83 to 7.27 and from 10.4 to 7.67, respectively. The AC treatment significantly varied ($p<0.05$) with the rising OM concentration, and pH in the ceramic, zeolite, and furnace slag treatment decreased more significantly ($p<0.05$) in the low (0% to 8%) than in the high (8% to 16%) OM treatments. P removal efficiency of AC was significantly inhibited ($p<0.01$) when the OM content rose from 0% to 16%. However, the P removal efficiencies of the furnace slag and ceramic were significantly inhibited ($p<0.05$) at higher OM contents, while that of the zeolite was only significantly inhibited ($p<0.05$) at lower OM contents (0% to 8%).

OM accumulations were common in both the natural wetlands and the CWs [11, 33-34]. Moshi et al. [35] and Christoph and Klaus [36] showed that P adsorption was inhibited by OM. Furthermore, Erich et al. [37] provided the following theories: 1) OM competes for sorption sites, 2) OM can release previously adsorbed P, and 3) OM can reduce the electrostatic attraction between the sorption sites and P. However, the present study verified that P adsorption capacities of the substrates could also be affected by pH, which could be influenced by added OM. Gray et al. [38] reported that P sorption is decreased due to substrates with greater amounts of Ca at lower pH values, and becomes higher at lower pH due to substrates with greater amounts of Al and Fe. Ann et al. [24] and Ugurlu and Salman [29] also reported that the precipitation of Al P and ferric P may increase at lower pH values, and lower pH values would result in lower dissolved Ca and Mg. The constant decreases in the P sorption capacities of the tested substrates at lower OM contents were mainly attributed to lower dissolved Ca concentrations at low pH and the theories presented by Erich et al. [37]. However, for the zeolite, ceramic, and furnaces slag substrates, the significant ($p<0.05$) decreases in P sorption of furnace slag and ceramic at high OM contents (16%) and slight ($p<0.05$) decreases in P sorption of ceramic could only be attributed to higher Al and Fe dissolution at lower pH. P sorption efficiency significantly decreased when the OM content was high (16%) because of the higher equilibrium pH, which was not low enough for Fe and Al dissolution [24, 38]. Thus, the P sorption capacities of the substrates

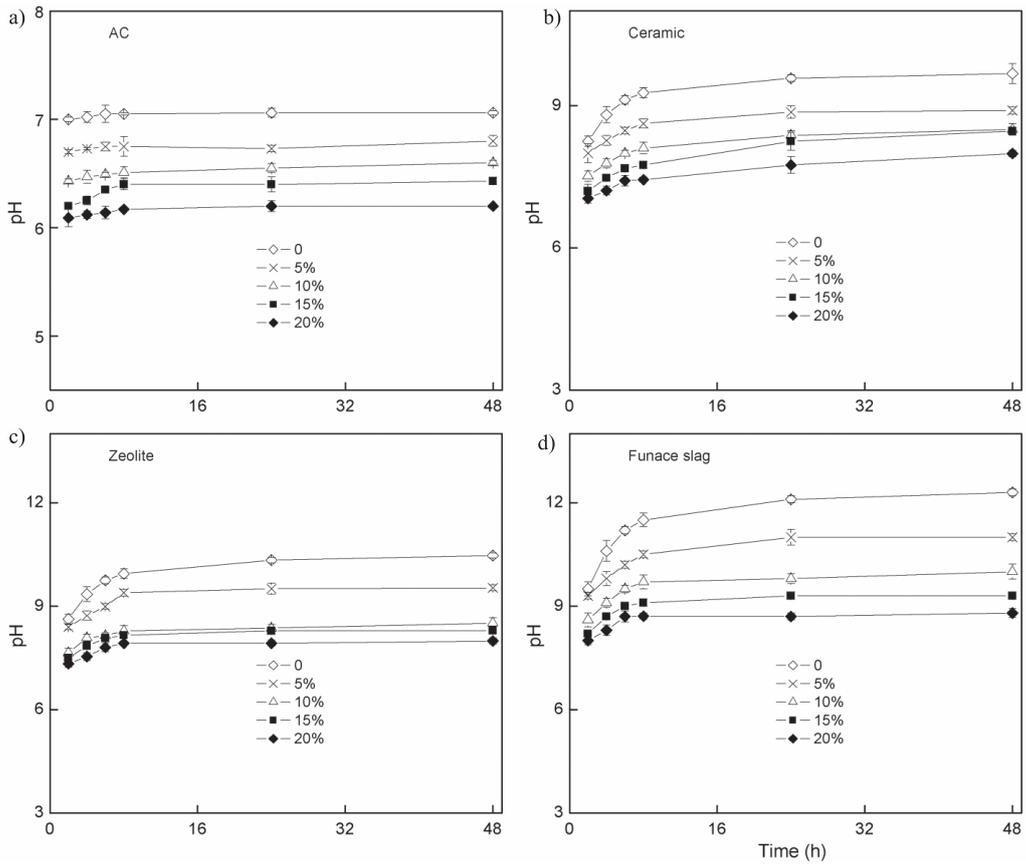


Fig. 2. Changes in pH with the OM levels.

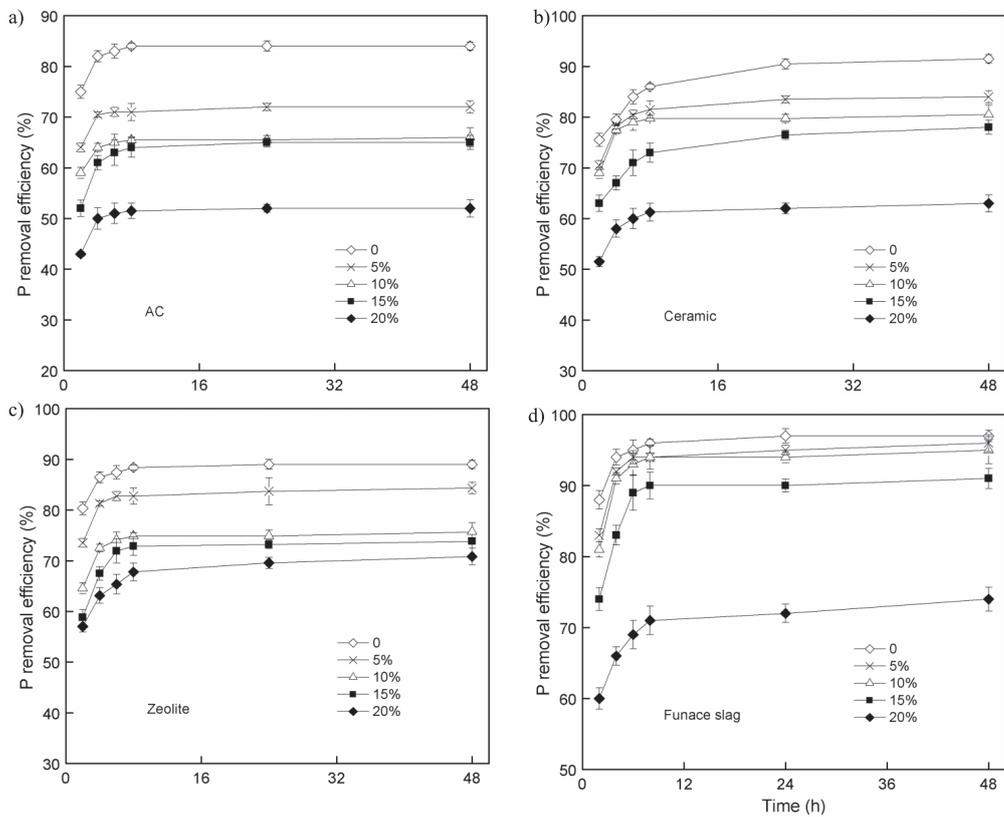


Fig. 3. Changes in P removal with OM levels.

Table 6. The proper selection of the substrates for treatment of wastewater with different characteristics.

The proper substrates	Characteristics of the wastewater				Costs/ (\$ kg ⁻¹)
	P concentration ↓ ^a , OM ↓	P concentration ↑ ^b , OM ↓	P concentration ↓, OM ↑	P concentration ↑, OM ↑	
Quartz sands	+++ ^c	+	++	+	0.2-0.4 [31]
AC	+	+++	+	+	0.6-0.8 [10]
Zeolite	+	++	+++	+++	0.9-1.6 [38]
Ceramic	+	++	++	++	0.4-0.7 [38]
Furnace slag	+	+++	+	++	0.8-1.7 [10]

^a↓: relatively low concentration.

^b↑: relatively high concentration.

^c+: the number of “+” shows the feasibility of the substrate for treatment of certain wastewater.

were also impacted by OM by influencing the pH. The substrates that contained higher Fe and Al contents and lower Ca contents should be chosen (e.g., zeolite) when the OM concentration in the wastewater is high.

The Proper Principles for Selecting Substrates

According to the P adsorption capacities of the tested substrates and the impact of the specific surface area and grain size, and Ca, Mg, Fe, Al, and OM contents on the P sorption capacities of these substrates we investigated, the proper principles for selecting substrates should be as follows. 1) For treatment of wastewater with simultaneous low P concentration and low OM, substrates with a low cost (for example, the quartz sands) should be chosen; 2) for treatment of wastewater with a high P concentration and low OM, substrates with a high P sorption capacity and relatively low cost should be chosen (OM accumulation resistance of the substrates does not have to be considered); 3) for treatment of wastewater with a low P concentration and high OM, only OM accumulation resistance and the cost of the substrates should be considered; and 4) for treatment of wastewater with simultaneous low high P concentration and high OM, substrates with high P sorption capacities and high OM accumulation resistance of the substrates should be considered (for example, zeolite and ceramic). The evaluation for proper use of the tested substrates is shown in Table 6, which provides a qualitative analysis for the selection process for substrates used for the treatment of wastewater with different characteristics. Thus, additional studies should be conducted to quantify the exact concentration range of P and OM suitable for different substrates.

Conclusions

We tested and evaluated P sorption properties of four quartz sands with different physicochemical characteristics and four substrates commonly used in CWs. Our results support the following conclusions:

- 1) The P sorption capacity decreased as follows: furnace slag > ceramic > zeolite > AC > quartz sands (IV > I > II > III), and the P adsorption capacities were correlated with the physicochemical characteristics of certain substrates.
- 2) The chemical precipitation of P by the substrates containing Fe was more effective than those containing Ca at the same content.
- 3) OM affects P adsorption of the substrates by influencing pH, and the substrates containing higher Fe and Al concentrations and lower Ca concentrations were more resistant to decreases in the P adsorption capacity due to the accumulation of OM.
- 4) Suitable substrates should be chosen for certain wastewater according to P sorption capacity, OM accumulation resistance, and cost.
- 5) Further study should be conducted to quantify the exact concentration range of P and OM that are suitable for different substrates.

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