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White hard clam (*Meretrix lyrata*) shells as novel filter media to augment the phosphorus removal from wastewater

T.A.H. Nguyen ^a, H.H. Ngo ^{b,*}, W. S. Guo ^b, T.T. Nguyen ^c, N.D. Vu ^{d,f}, S. Soda ^c,
T.H.H. Nguyen ^d, M.K. Nguyen ^d, T.V.H. Tran ^a, T.T. Dang ^a, V.H. Nguyen ^e, T.H. Cao ^{a,f}

^a Vietnam Japan University (VNU-VJU), Vietnam National University, Hanoi, Luu Huu Phuoc St., Nam Tu Liem Dist., Hanoi 101000, Vietnam

^b Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology, Sydney, Broadway NSW 2007, Australia

^c Graduate School of Science and Engineering, Ritsumeikan University (RITs), Biwako-Kusatsu Campus, Shiga 525-8577, Japan

^d University of Science (VNU-HUS), Vietnam National University, Hanoi, 334 Nguyen Trai Rd., Thanh Xuan Dist., Hanoi 120106, Vietnam

^e Research Center for Environmental Monitoring and Modeling, VNU University of Science (VNU-HUS), 334 Nguyen Trai Rd., Thanh Xuan Trung Ward, Thanh Xuan Dist., Hanoi 120106, Vietnam,

^f Center for Environmental Technology and Sustainable Development, VNU University of Science (VNU-HUS), 334 Nguyen Trai Rd., Thanh Xuan Trung Ward, Thanh Xuan Dist., Hanoi 120106, Vietnam,

* Corresponding author: *E-mail address:* ngohuuhaol21@gmail.com

Abstract

It is well recognized that filter media play a crucial role in constructed wetlands (CWs) for decontamination of phosphorus (P)-rich wastewater. This study investigates the suitability of raw white hard clam shells (WHC) and white hard clam shells thermally modified at 800 °C (WHC-M800) as potential media to enhance P treatment performance in CWs. The results indicated that both WHC and WHC-M800 displayed appropriate physicochemical properties, such as high porosity, excellent hydraulic conductivity, and rich Ca content. WHC-M800 exhibited a superior P adsorption capacity (38.7 mg/g) to WHC (12.8 mg/g). However, the practical utilization of WHC-M800 as filter media in CWs may be compromised, due to certain limitations, for example: extremely high pH values in the post-adsorption solutions; high weight losses during calcination and adsorption processes; low mechanical strength; and intensive energy consumption. In contrast, the WHC demonstrated significant advantages of reasonably high P adsorption capacity, locally abundant availability, low cost, and marginal side effects. The fractionation of inorganic P of WHC and WHC-M800 revealed that

Ca-bounded P was the most dominant binding form, followed by loosely bound P, Fe-P, occluded P, and Al-P. The present study demonstrates that recycling of WHC shells as a potential substrate in CWs provides a feasible method for upgrading P removal in CWs. Additionally, it helps to reduce waste WHC shells in a simple, cheap, and eco-friendly way, thus can double environmental benefits.

Keywords: Ca-rich materials; Constructed wetlands; Filter media; Phosphorus removal; White hard clam (*Meretrix lyrata*)

1. Introduction

In Vietnam, pig farming plays an important role, accounting for 60% total value of the livestock sector (Nguyen et al., 2019). On one side, it contributes to improving the income of the rural residents. On the other side, it generates a huge amount of swine wastewater. Though swine wastewater is typically treated using anaerobic digestion, the effluent is often of poor quality. The concentrations of the main pollutants e.g. organic matters, nitrogen (N), phosphorus (P), and pathogen in the swine wastewater after anaerobic digestion exceed the permissible levels (QCVN 40:2011/BTNMT, Column B) dozens to hundreds of times (Ho et al., 2016). Therefore, additional and enhanced treatment of anaerobically digested swine wastewater is now vitally important in Vietnam.

So far, many technologies have been applied for decontamination of anaerobically digested swine wastewater, namely chemical precipitation, coagulation, ion exchange, biological trickling filtration, bio-products, and algae culture pond (Bunce et al., 2018). However, these technologies have such drawbacks as intensive chemical use, sludge generation, expertise requirement, high cost, or poor efficiency (Patil Mansing and Raut, 2013). Conversely, constructed wetlands (CWs) are known to have significant advantages, such as low cost, simple operation, low energy input, and desirable treatment efficiency (e.g. total suspended solid (TSS), organic matters, and N), high biodiversity value, and great reuse

potential of nutrients (Almuktar et al., 2018; Chan et al., 2008). Nevertheless, the widespread application of CWs is still restricted due to the low and unstable P removal efficiency (32.0-78.4%) (Vohla et al., 2011). It has been well recognized that substrates played a major role in P removal in CWs (Wu et al., 2013). The P removal percentage in CWs without using reactive filter media (containing high metal oxides content) was limited to 40-60% (Bunce et al., 2018). Yet the use of dolomite as a special filter material improved the total P removal by 21% compared to sand as a conventional filter media (Žibienė et al., 2015). The P sequestration ability of a filter material greatly relied on its contents of Ca, Mg, Fe, and Al oxides (Cucarella and Renman, 2009). Obviously, unsatisfactory P removal in CWs can be overcome by adding P-retentive amendments (Ballantine & Tanner, 2010).

Recently, the recycling of wastes/by-products as P adsorbents has drawn much attention. Of which, seashells exhibited significant merits, such as abundant CaO content, no toxicity, and recyclability as P-rich soil amendments after saturation (Nadeem, 2018). Kwon et al. (2004) reported that raw oyster shells could barely remove P, whereas the pyrolysed oyster shells removed up to 98% and the latter were notably cheaper than other P treatment chemicals. As reported by See et al. (2015), when the content of oyster shells rose the saturation time of the filter medium was prolonged. These studies indicate a great potential to explore seashells as filter media to upgrade P removal in CWs.

In Vietnam, white hard clam (*Meretrix lyrata*) shell is a waste/by-product from marine culture and the seafood processing industry. Together with clam processing, an enormous amount of clam shells is generated annually (> 300,000 tons) (Nguyen, 2019). As well the clam shells decompose only with great difficulty in nature. Consequently, it poses a big challenge for solid waste disposal in Vietnam's coastal provinces. Globally, seashells can be recycled for multi purposes such as construction materials, animal feed additives, artificial bone, and catalysts for bio-diesel production, bactericidal agents, dehalogenation agents, acid gas cleaning, low-cost adsorbents, and soil amendments (Yao et al., 2014). However, in

Vietnam the largest amount of clam shells is dumped in unsanitary landfills while other usages are minor (Ngo et al., 2017). In addition, massive and widespread death of cultured clams has been reported frequently in the coastal provinces of Vietnam as a result of water quality deterioration and climate change (Bui and Tran, 2013). Due to the lack of proper disposal, clam shells with meat leftover cause serious odor pollution and require a large land area for landfilling (Yao et al., 2014). Therefore, an innovative recycling of clam shells is urgent so that this abandoned waste can be turned into a beneficial product while its adverse environmental impacts are minimized.

In short, it is clear from the literature review that so far seashells are normally investigated as P adsorbents. It is still lack of studies exploring them as the wetland filter media. Consequently, while P sorption capacity received much attention of scientists, other hydraulic and mechanical properties of the materials, which are essential for CWs' sustainable operation, were usually ignored. This may lead to inappropriate justification when the screening of filter materials for use in CWs is made.

The present study aims at investigating the applicability of WHC and WHC-M800 as the wetland filter materials to augment the P removal from synthetic wastewater. The focus was placed on examining adsorption behaviors and other critical physiochemical properties. By recycling of WHC as a wetland substrate, it is expected to achieve multiple environmental and economical purposes, such as intensifying P-rich wastewater purification, mitigating odor pollution and minimizing the waste WHC disposal in a feasible, economic and environmentally friendly way.

The novelty of this work can be seen from its use of a modified, simple scoring system that enabled the quantitative evaluation of the media's applicability. In addition, a comprehensive evaluation of was performed based on a wide variety of criteria covering all technical, environmental and economic aspects of the filter media. Finally, to the best of the authors' knowledge, this is the first time WHC has been explored as the wetland filter media

to intensify P decontamination in the P-rich wastewater like swine wastewater after anaerobic treatment.

2. Materials and methods

2.1. Materials

White hard clam (*Meretrix lyrata*) shells were collected from Thai Binh Shellfish Co., Ltd. in Nam Think commune, Tien Hai district, Thai Binh province, which has the highest hard clam farming area and clam output (1,984 ha and 30,130 tons/year) in Vietnam (Bui and Tran, 2013). Following this, clam shells were washed with tap water (1 m³/ton) to remove meat leftover, and then left to dry in the sun. Subsequently, clam shells were ground with a stone crusher (NHHP PEX 15, Vietnam) and sieved with a sieve shaker (AS 200, Retsch, EU) to get the desirable particle size (1.4-2 mm). This particle size was used in all experiments in this study. Later, the ground white hard clam shells were heated at three categories of temperatures (750, 800, and 850 °C) with little oxygen in the furnace (CWF 12/13, Carbolite, England) to determine the optimal calcination temperature. The calcined clam shells were referred as WHC-M750, WHC-M800, and WHC-M850, respectively. Finally, the calcined clam shells were cooled down in a furnace to room temperature (25 °C), then removed and stored in a tight glass bottle for further investigations.

2.2. Chemicals

All reagents in this study were purchased from ESQ Co., Ltd. (Ba Dinh district, Hanoi). These chemicals were all AR grade. The P solutions of different concentrations were prepared by dissolving appropriate amounts of KH₂PO₄ into distilled water.

2.3. Wastewater

In this work, the real anaerobically digested swine wastewater was collected from a large-scale pig farm, which was located in Luong Xa village, Nam Dien commune, Chuong My district, Hanoi (Coordinates: 20°53'49.6"N 105°42'57.9"E). The chemical composition of the real wastewater was characterized as follows: pH 8.1±0.3, BOD₅ 299±48 mg/L, COD

1560±308 mg/L, total N (TN) 730±82 mg/L, total P (TP) 151±26 mg/L, NH₄-N 571±38 mg/L, PO₄-P 52.9±7 mg/L, and turbidity 748±57 NTU. The real wastewater was utilized only for the test to compare the P removal efficiency in the real wastewater and P aqueous solutions.

The P aqueous solutions were prepared by dissolving KH₂PO₄ in tap water at proper mixing ratios to get desirable concentrations. The P solutions were utilized in the experiments to investigate influential factors, isotherms, kinetics, and a comparative study on P removal efficiencies of the filter media (WHC and WHC-M800) in the real wastewater and aqueous solutions.

2.4. Experimental methods

2.4.1. Characterization of filter materials

2.4.1.1. Physical properties

The hydraulic conductivities of WHC and WHC-M800 were determined based on Darcy's law, using a constant head permeability meter having the height (L) of a material layer of 30 cm, and the diameter of 10 cm. The water was let to flow upward direction through the tested material. The flow rate (Q) was measured for each head pressure. The hydraulic conductivity of the filter material was expressed in Eq. 1 as follows (Stapleton and Mihelcic, 2001).

$$Q = \frac{K \cdot A \cdot \Delta h}{L} \quad (\text{Eq. 1})$$

where Q is the flow rate (m³/s); K is the saturated hydraulic conductivity (m/s); Δh is hydraulic head pressure (m); L is length of the tested material layer (m); A is the cross-sectional area of the column (m²).

Porosities of the materials were determined with a procedure adapted from Nguyen (2019). Specific surface area, pore size and pore volume of the materials were measured using adsorption and desorption techniques with TriStar II Plus (Micromeritics-America). The materials' surface morphology and microstructure were imaged using Avomeen's SEMTech

Model 1830 SEM/EDS in the laboratory of Institute of Chemistry, Vietnam Academy of Science and Technology (VAST).

2.4.1.2. Chemical properties

Key functional groups on the surface of WHC and WHC-M800 were characterized by IR analysis. FT-IR spectra were recorded on 6300 typeA FT-IR spectrometers with a resolution of 1 cm^{-1} in the range from 4000 cm^{-1} to 400 cm^{-1} . Chemical compositions of the materials were defined by X-ray fluorescence analyzer (WD-XRF, S4 Bruker, Germany) at the Institute of Geological Sciences (IGS), Vietnam Academy of Science and Technology (VAST).

2.4.2. Adsorption tests

A stock P solution (1000 mg/L) was prepared by dissolving a proper amount of KH_2PO_4 in the distilled water produced with a double distilled water machine (A4000D, Bibby, England). The desired working solutions were made by diluting the stock solution. All batch experiments were conducted with a particle size range of 1.4-2 mm, in Erlenmeyer flasks on the orbital shaker (OS-3000, HACH) at the same speed (120 rpm) and temperature ($25\text{ }^\circ\text{C}$). Phosphorus concentrations were analyzed using UV-VIS Spectrophotometer (Unico, S2150UV) according to U.S. EPA method 365.2. All experiments were done in triplicate and the mean value was calculated. Furthermore, the pH values of post-adsorption solutions were measured using a pH meter (Mettler Toledo Seven Compact S220K, Switzerland).

2.4.2.1. Influential factors to P adsorption

In order to investigate factors influencing P adsorption onto the WHC and WHC-M800, adsorption tests were implemented by varying the influential factors while keeping other conditions the same as mentioned above. The pH values of initial P concentration were varied in the 3-11 range using HCl and NaOH of various concentrations. Different temperatures were used including 25, 30, 35, and $40\text{ }^\circ\text{C}$. The adsorbent dose was altered from 0.5 to 5.0 g/75 mL.

2.4.2.2. Isotherm study

Adsorption isotherm characteristics were studied by varying the initial P concentrations (2.5, 5, 10, 25, 50, 100, 200, 400, 500, 800, 1000 mg/L) at the optimal pH value of 3 (pH was adjusted using HCl). Following adsorption, the suspension was filtered through a 0.45 μm filter paper (Advantech, Japan), and the filtrate was used for P determination using UV-VIS Spectrophotometer (Unico, S2150UV). The adsorbed P amount was calculated by the difference between initial and residual P concentrations. The adsorption capacity at equilibrium was estimated as follows:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (\text{Eq. 2})$$

where C_i (mg/L) and C_e (mg/L) stand for the initial and equilibrium P concentrations, respectively, V (L) represents the solution volume, and m (g) indicates the adsorbent weight.

The isotherm study generates information on the adsorption capacity of an adsorbent. The maximum adsorption capacity is a key factor in screening potential substrates for use in CWs to upgrade the removal of P. In order to determine this parameter, the Langmuir isotherm model is commonly used. The linear equation of the Langmuir isotherm model was described as follows (Nguyen, 2015):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (\text{Eq. 3})$$

where q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) represents Langmuir constant associated with the affinity of binding sites on material, q_e (mg/g) indicates the adsorption capacity, and C_e (mg/L) is the concentration of P in solution at equilibrium. R^2 is the correlation coefficient. The values of q_m , K_L and R^2 can be calculated from the slope and intercept of the linear plot of $1/q_e$ versus $1/C_e$.

In an attempt to identify which isotherm model is more suitable in describing the P adsorption processes of the materials, Freundlich isotherm model was also applied to fit experimental data. The linear equation of Freundlich model was described by Eq. 4 (Behnamfard and Salarirad, 2009; Nguyen, 2015).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{Eq. 4})$$

where K_F and $1/n$ are Freundlich constants indicating adsorption capacity and adsorption intensity of the adsorbent, respectively. The unit of K_F is $(\text{mg/g})(\text{L/mg})^{1/n}$. q_e (mg/g) and C_e (mg/L) represent the quantity of phosphate adsorbed on adsorbent and the concentration of P in solution at equilibrium, respectively. The values of K_F , n , and R^2 of Freundlich isotherm model can be determined from the slope and intercept of the linear plot of $\ln q_e$ versus $\ln C_e$.

2.4.2.3. Kinetic study

The kinetic tests were conducted in conical flasks. Each one corresponds to a given adsorption time. Each flask containing 75 mL of the solution of 50 mg P/L was added 3 g of WHC with the particle size of 1.4-2 mm. All flasks were shaken on an orbital shaker (OS-3000, HACH) at the speed of 120 rpm and temperature of $25 \pm 1^\circ\text{C}$. At different interval adsorption times from 2 to 26 hours, each suspension was filtered through 0.45 μm pore size filter paper. The obtained filtrates were analyzed to determine the remaining concentration of P. The similar procedure was conducted for WHC-M800, excepting for the differences in adsorbent doses (0.5 g/75 mL) and sampling times (from 0.1 to 4.5 hours).

Two most popular adsorption kinetic models (the Pseudo-first-order and the Pseudo-second-order kinetic models) were used for fitting the experimental data. The linear expressions of these models were expressed by Eqs. 5 & 6, respectively (Nguyen, 2015):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (\text{Eq. 5})$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\text{Eq. 6})$$

where k_1 (h^{-1}) and k_2 ($(\text{mg/g})^{-1}\text{h}^{-1}$) are adsorption rate constants of the first and second order models, respectively; q_t and q_e are the amounts of P adsorbed on 1 gram of the adsorbent at time t and at the equilibrium, respectively; t (h) is the adsorption time. k_1 can be determined from the slope of the linear plot of $\ln(q_e - q_t)$ versus t , whereas k_2 can be calculated from

the intercept of the linear plot $\frac{1}{(q_e - q_t)}$ versus t . q_t and q_e were calculated using Eqs. 7 & 8

as follows:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (\text{Eq. 7})$$

$$q_e = \frac{(C_i - C_e)V}{m} \quad (\text{Eq. 8})$$

where C_i , C_t , C_e (mg/L) are P concentrations at initial, t , and the equilibrium times, respectively, V (L) is volume of adsorption solution, and m (g) is the weight of the adsorbent.

All adsorption experiments were performed under the conditions summarized in Table S1.

2.4.3. Fractionation of inorganic phosphorus binding forms in the spent filter media

This experiment was designed to understand inorganic P binding forms, and subsequently the P removal mechanisms of WHC and WHC-M800. It was implemented through the strategy of sequential extractions, using procedures modified from Deng and Wheatley (2018) and Korkusuz et al. (2007). As is shown by Table 1, 1 g of the filter material, which had been adsorbed P in advance under the conditions (C_i 50 mg/L, 24 h, 120 rpm, 25 °C), was utilized for sequential extraction experiments. The extracted solutions were analyzed to identify P contents.

Table 1

Procedure for extraction of inorganic P binding forms in 1 g of sample.

Phosphorus fraction	Extractant	Treatment
Loosely bounded P (LBP)	1 M NH_4Cl	50 mL, shaking 1 h
Al-P	0.5 M NH_4F (pH = 8)	50 mL, shaking 1 h
Fe-P	0.1 M NaOH	50 mL, shaking 18 h

Ca-P	1 M H ₂ SO ₄	50 mL, shaking 1 h
O-P	CDB (pH = 7.6)	45 mL, shaking 1 h

Source: Korkusuz et al. (2007).

Notation: CDB: 0.3 M Na₃C₆H₅O₇ (Sodium citrate-sodium dithionite-sodium bicarbonate) + 1 M Na₂S₂O₄ + 1 M NaHCO₃.

2.4.4. Treatment performance of the filter media in real wastewater

This experiment examined the P treatment performance of WHC and WHC-M800 in real wastewater scenarios. The anaerobically digested swine wastewater was collected from a large-scale commercial pig farm in Chuong My, Hanoi and analyzed to determine the orthophosphate and ammonium concentrations. Synthetic wastewater was prepared in the laboratory of the previously noted Master's Program in Environmental Engineering by simulating the orthophosphate and ammonium composition of the real wastewater. The pH of synthetic wastewater was adjusted to be the same as that of real wastewater using NaOH and HCl solutions. The adsorption tests were conducted using the following conditions: initial P concentration of 54 mg/L, adsorbent dose of 3 g/75 mL, pH of 7.44, shaking speed of 120 rpm, contact time of 24 h, temperature of 25 °C, and particle size of WHC and WHC-M800 of 1.4-2 mm.

2.4.5. Evaluating the applicability of the filter materials

For the objective of evaluating the suitability of WHC and WHC-M800 as filter media to intensify P removal in CWs, the current study utilized a simple additive scoring system, which was modified from Ballantine and Tanner (2010). There were two main differences between two scoring systems. Firstly, the present system used more evaluation criteria (10) than the old system (4) for allocating scores to the materials. Secondly, the present system gave higher weight to more important criteria. Accordingly, all criteria were divided into three groups according the descending order of significance including (i) the critical criteria, (ii)

less important criteria, and (iii) fundamental criteria. The criteria belonging to the group (i), group (ii), and group (iii) were allocated the weights of 3, 2, and 1, respectively. In contrast, the old scoring system considered all criteria to be equally significant. The similarity was that both scoring systems had three categories (high = 3, medium = 2, and low = 1) for all criteria. In the present study, for beneficial criteria (e.g. 1, 2, 3, 4, 5, 6, 9), high, medium, and low categories were allocated 3, 2, and 1 score(s), respectively. For harmful criteria (e.g. 7, 8, 10), the score allocation was in opposite, with 3, 2, and 1 score(s) for low, medium, and high categories. The criteria with the highest score (3) and the lowest score (1) were considered as advantages and disadvantages of the filter material, respectively. The cumulative score and the disadvantage/advantage ratio were used to place the two investigated filter materials in the suitability ranking order.

2.5. Statistical analysis

All tests were done in triplicate. Microsoft Office Excel 2010 (Microsoft, USA) was applied for analyzing all data with one-way analysis of variance (ANOVA). A significant difference was considered at the level of $p < 0.05$.

3. Results and discussion

3.1. Characterization of the filter materials

a. Porosity, hydraulic conductivity, BET surface area

The physical properties of WHC and WHC-M800 are presented in Table S2.

As Table S2 shows, the porosities of WHC and WHC-M800 were 43% and 45%, respectively. These values were even higher than that of the granular activated carbon (40%) (Al-Degs et al., 2008) or sand (30%) (Žibienė et al., 2015), which were known to operate in the continuous fixed-bed operation without water clogging. In this study, the hydraulic conductivities of WHC and WHC-M800 were 0.7 cm/s and 0.8 cm/s, respectively. These values are in the same order of magnitude as that of coarse sand (0.01-1 cm/s), a conventional substrate in CWs (Nguyen, 2019). After calcination, the pore size and pore volume of

WHC-M800 was increased, whereas BET surface area of WHC-M800 declined compared to those of WHC. The increment in the pore size of WHC-M800 was probably due to the destruction of nacre layer, change in lattice layer and the collapse of pore walls as a result of calcination (Zhang et al., 2013). The BET surface areas of WHC and WHC-M800 were lower than those of other seashells (Table S2). This can be attributed to the variation in physical structure of different species of seashells. However, Table S2 shows that the BET surface areas of filter materials did shrink with increasing pore sizes. A similar trend was reported by Li et al. (2005) for the nitric acid pre-treated activated carbon. Especially, the BET surface areas of WHC and WHC-M800 were dramatically smaller (2,645 and 11,714 times, respectively) than that of activated carbon. This meant that chemical sorption rather than physical sorption should be the dominant P removal pathway of both WHC and WHC-M800.

b. SEM-EDS analysis

SEM-EDS was employed to examine the surface morphology and chemical element composition of WHC and WHC-M800. SEM images and EDS spectra of WHC and WHC-M800 are illustrated in Fig. 1. According to Figs 1a and 1b, the morphology of WHC was altered after calcination. Specifically, more crystals appeared on the surface of WHC-M800 than raw WHC. It was assumed that these crystals on WHC-M800 were CaO, which were generated from thermal decomposition of CaCO_3 in the WHC. It is evident from Figs. 1c and 1d that both WHC and WHC-M800 were mainly composed of carbon (C), oxygen (O), and calcium (Ca). However, their percentages in WHC ($\text{C} > \text{O} > \text{Ca}$) were different from those in WHC-M800 ($\text{Ca} > \text{O} > \text{C}$). The percentage of C in WHC-M800 was diminished by 14.47% compared to that in WHC. In contrast, the percentages of Ca and O in WHC-M800 were escalated by 17.7% and 16.01%, respectively. As a result of calcination, CaCO_3 was converted into Ca and vaped CO_2 . Due to the weight loss in the form of CO_2 , the proportions of major elements (Ca, C, and O) was altered.

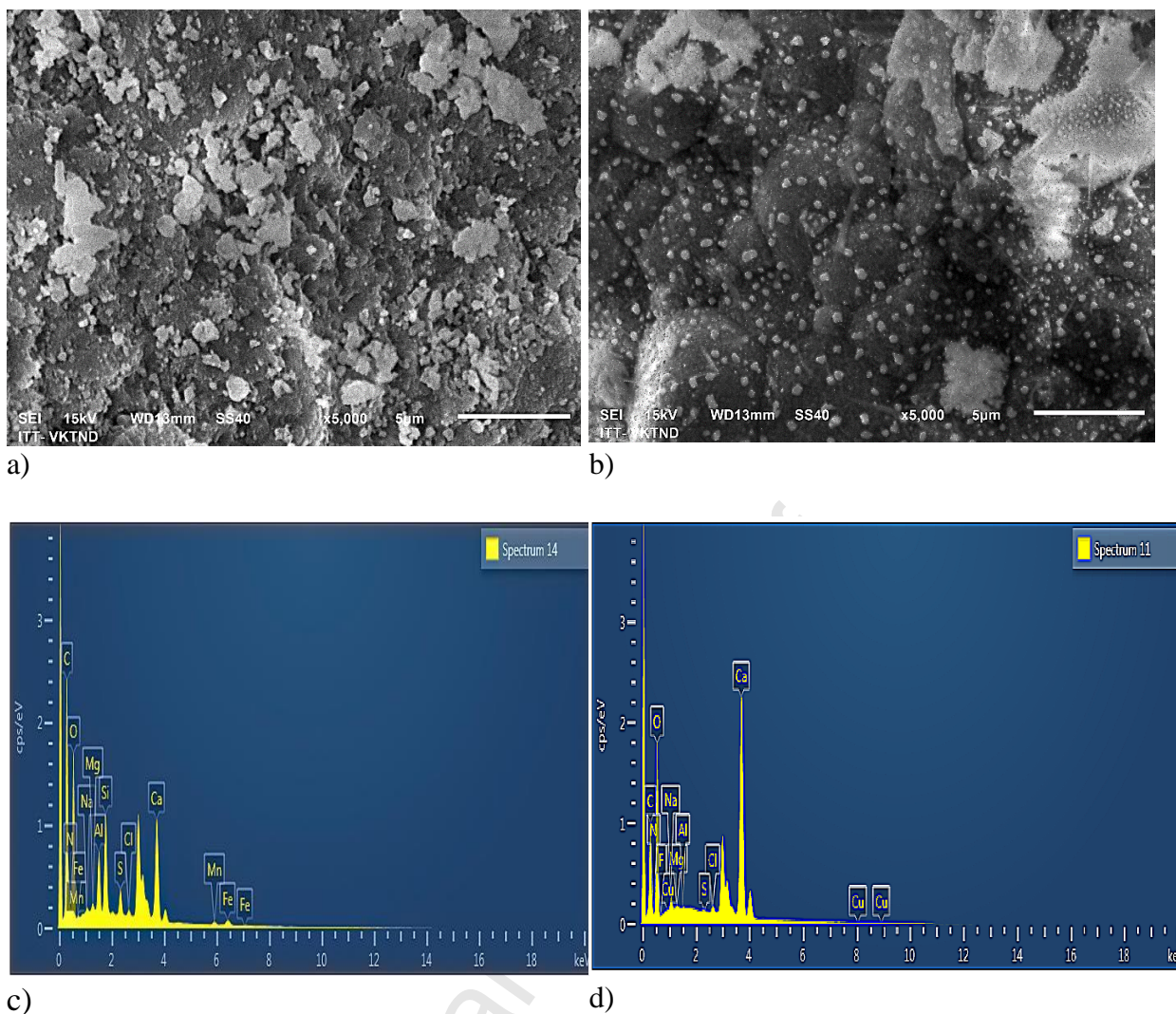


Figure 1

SEM images and EDS spectra of WHC and WHC-M800: a) SEM image of WHC, b) SEM image of WHC-M800, c) EDS spectrum of WHC, and d) EDS spectrum of WHC-M800.

The chemical compositions of WHC and WHC-M800 are given in Table 2. It can be observed that CaO was the most abundant constituent in both WHC (53.92%) and WHC-M800 (56.38%) while other metal oxides (MgO, Fe₂O₃, and Al₂O₃) were marginally available (< 0.1%). The percentages of CaO in WHC and WHC-M800 were more or less comparable to those in other Ca-rich materials, such as commercial limestone and some categories of bivalve shells, for example oyster shells, mussel shells. Because of CaO's abundance, these materials should possess good P binding capacities, thus can become potential adsorbents for P elimination from wastewater (Cucarella and Renman, 2009).

Besides, as a result of minor amounts of other metal oxides, there is no danger of releasing toxic heavy metals into aquatic solutions when WHC and WHC-M800 are utilized for wastewater purification. In other words, the health risk of using WHC and WHC-M800 as P adsorbents should be negligible.

Table 2

The main metal oxides contents of WHC, WHC-M800 and other Ca-rich materials.

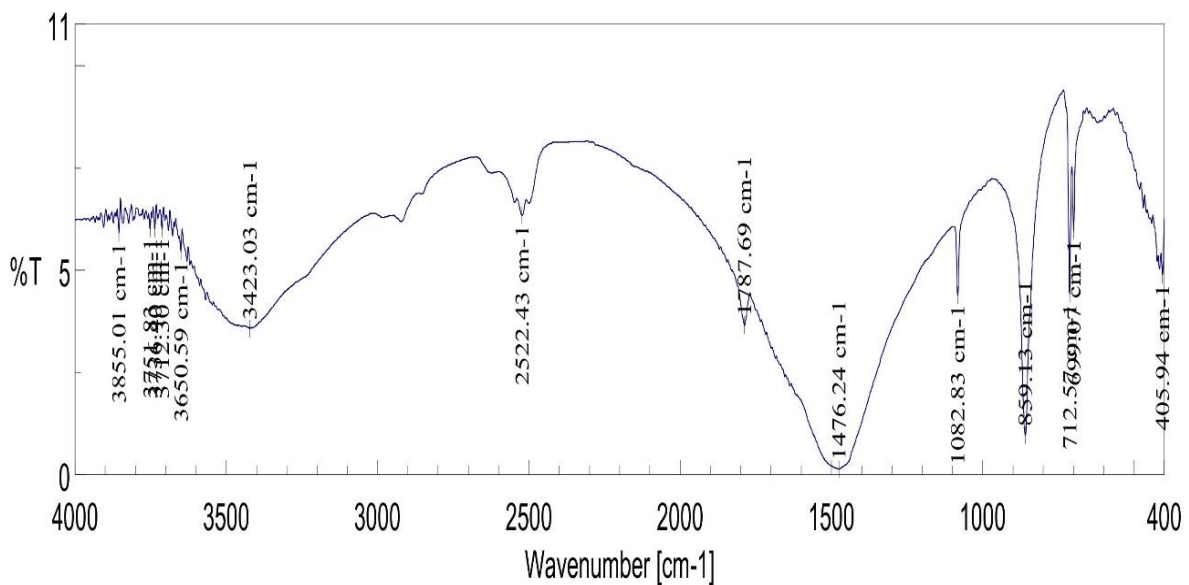
Material	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	Reference
WHC	53.92	0.07	< 0.01	0.02	This study
WHC-M800	56.38	0.08	< 0.01	0.02	This study
Oyster shell	51.06	0.51	0.50	0.20	Yao et al., 2014
Mussel shell	53.70	0.33	0.13	0.03	Yang et al., 2005
Limestone	54.70	0.25	0.07	0.12	Jung et al., 2005

c. FTIR analysis

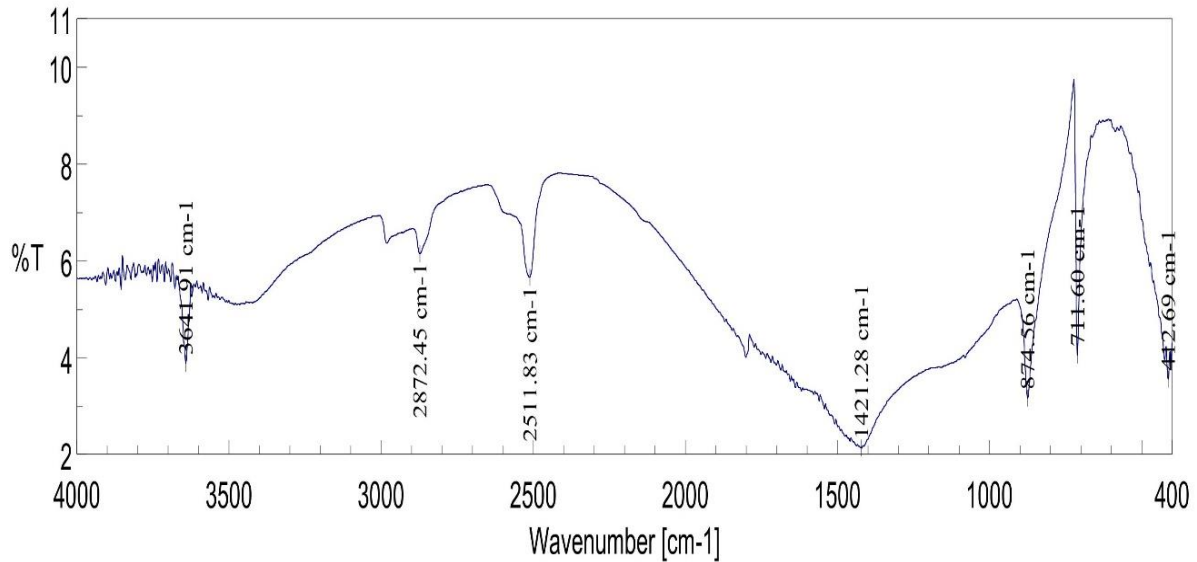
The functional groups of WHC and WHC-M800 were examined using Fourier transform infrared (FTIR)-6300 typeA. The FTIR spectra of these filter materials were recorded in the wavenumber range of 4000 – 400 cm⁻¹. Fig. 2a represents the FTIR spectrum of WHC. It can be seen that the peaks at the wavenumbers of 712.53, 859.13, 1082.83, 1787.69 and 2522.43 cm⁻¹ were dominant, indicating the presence of CO₃²⁻ groups in this material (Khiri et al., 2016). The FTIR spectrum of WHC-M800 is shown in Fig. 2b. It can be observed from Fig. 2b that the FTIR spectrum of WHC-M800 had the same peaks of carbonate groups as those of WHC at bands of 711.60, 874.56, 1787.69, and 2511.83 cm⁻¹. Nevertheless, the intensities of these peaks in WHC-M800 were lower than those in WHC. This can be explained by the fact that, as a consequence of thermal treatment of WHC, CaCO₃ was converted into CaO and CO₂ emitted into the air, leading to a reduction in the number of carbonate groups in the

calcined product as WHC-M800. Similar findings were reported by Kim et al. (2018) for P adsorption on calcined cockle shells.

The peak of OH⁻ group could be found in the FTIR spectra of both WHC and WHC-M800. However, the peak intensity of WHC-M800 was higher than that of WHC. This is probably due to the fact that Ca existed mainly in the form of CaO in WHC-M800, whereas CaCO₃ was a major component of WHC. Since CaO could adsorb H₂O better than CaCO₃, WHC-M800 displayed more OH⁻ groups compared to WHC (Ngo et al., 2017). As a result of the chemical reaction between CaO (solid) and H₂O to form Ca(OH)₂ (suspension) the mechanical strength of WHC-M800 can be reduced in comparison with WHC, thereby hindering its sustainable use as a filter media in CWs. The results implied that WHC-M800 should be kept in a tight glass bottle to avoid undesirable sorption of water vapor.



a)



b)

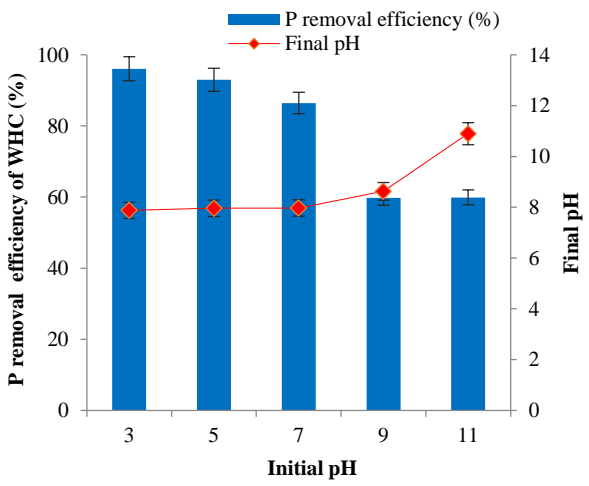
Figure 2

FTIR spectra of a) WHC and b) WHC-M800.

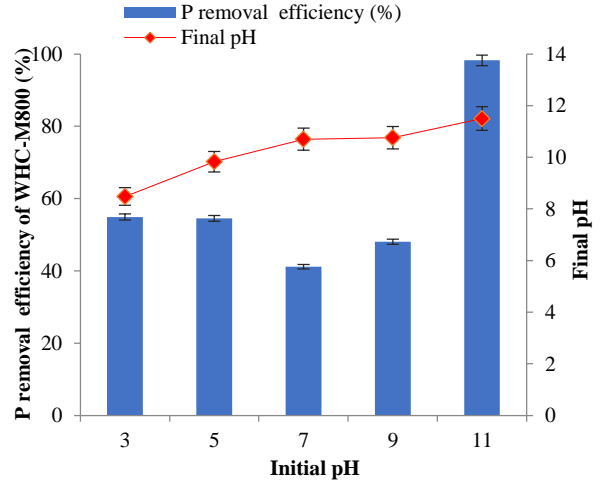
3.2. Factors influencing P adsorption

3.2.1. The effect of pH

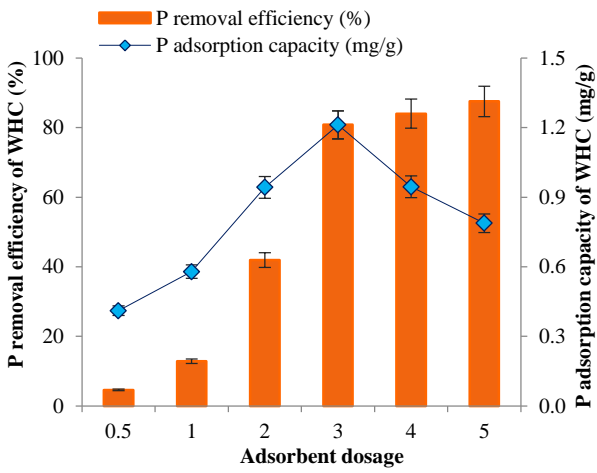
pH plays an important role in P adsorption. That is because the ionization of active functional groups on adsorbent surface and the speciation of P are affected by pH (Wang et al., 2015). Hence, this experiment was implemented to explore effects of the solution pH on the P removal efficiency of WHC and WHC-M800. The finding may be useful for preparing the simulated anaerobically digested swine wastewater for use in adsorption tests later. The data are illustrated in Fig. 3.



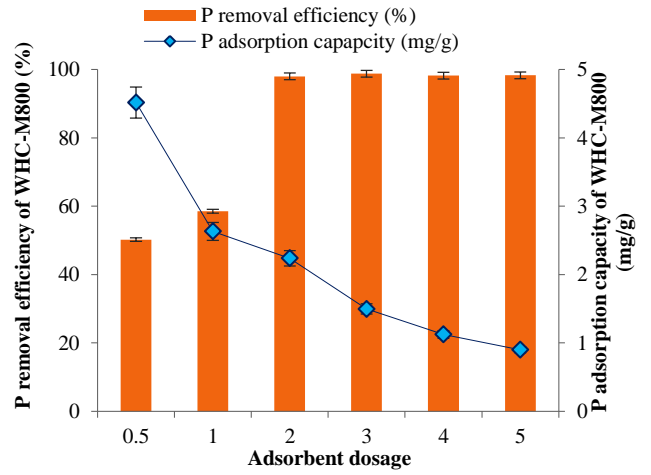
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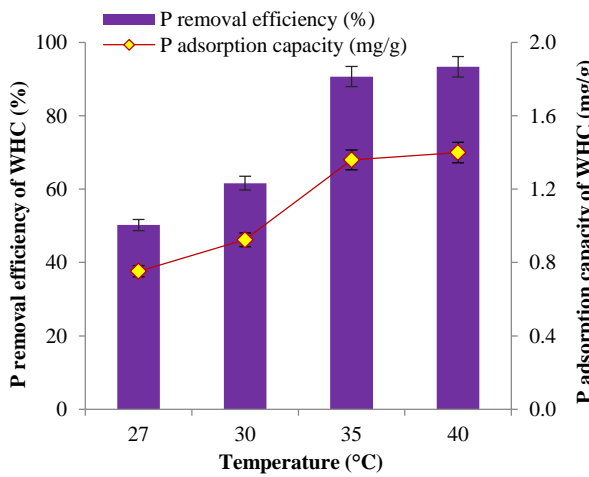
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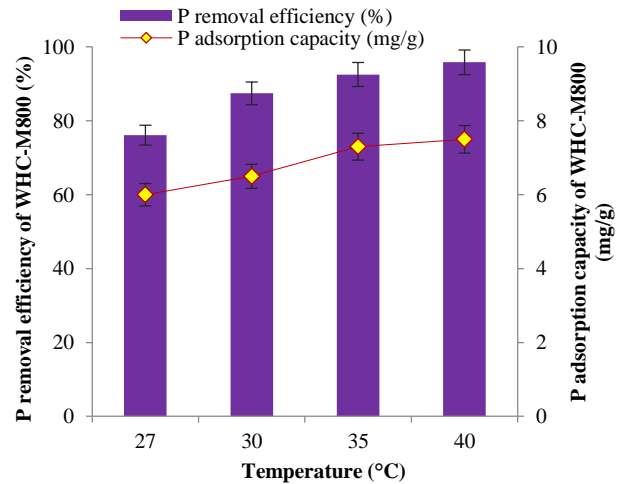
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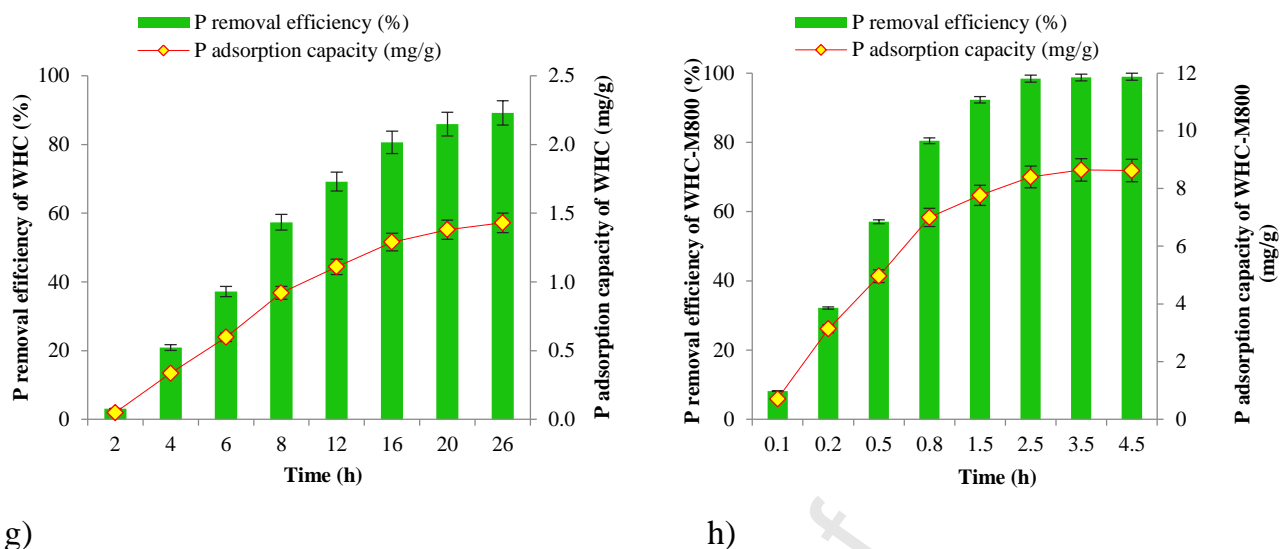


Figure 3

Factors influencing P adsorption capacity and P removal efficiency of WHC and WHC-M800: a) pH on WHC, b) pH on WHC-M800, c) Adsorbent dose on WHC, d) Adsorbent dose on WHC-M800, e) Temperature on WHC, and f) Temperature on WHC-M800, g) Contact time on WHC, and h) Contact time on WHC-M800.

Figs. 3a and 3b show the effects of pH on P removal of WHC and WHC-M800, respectively. As is shown in Fig. 3a, WHC exhibited the highest P removal efficiency (96%) at the pH value of 3. The P removal efficiency of WHC declined when the pH level increased. The P removal efficiencies at pH values of 9 and 11 (59.81% and 59.90%, respectively) were noticeably lower than that at a pH value of 3 (96.08%). This finding is consistent with those reported by Patil Mansing and Raut (2013) and Yeom and Yung (2009) for laterite and scallop shells, respectively. The trend can be explained by the two following mechanisms, namely electrostatic interaction and precipitation. Firstly, in the acidic medium, positive H^+ cations in the aqueous solution were attached to the surface of WHC, creating a secondary positive layer to bind the negative PO_4^{3-} anions. Secondly, the acidic medium made it possible for WHC to release more positive Ca^{2+} cations into solution, which reacted with negatively charged PO_4^{3-} anions to form the precipitation of $Ca_3(PO_4)_2$. Conversely, in the alkaline

medium, as a result of attachment of OH^- anions to WHC surface, a negatively charged OH^- layer was generated. Due to the electrostatic repulsion force between OH^- on the WHC surface and PO_4^{3-} in the aqueous solution, the retention of P by WHC was diminished. It can be seen from Fig. 3b, the similar trend occurred for WHC-M800 in the pH range of 3-7. However, the P removal efficiency of WHC-M800 rose sharply in the pH range of 9-11, reaching an extremely high percentage (98.24%). This can be attributed to the dominance of precipitation over the adsorption as the major P removal mechanism. The precipitate was formed by the reaction of Ca^{2+} cations, which were released from thermally modified WHC, with PO_4^{3-} anions in the solution. This assumption is confirmed by the observation of a thick layer of white precipitate at the bottom of conical flasks after adsorption (Deng and Wheatley, 2018).

In short, both WHC and WHC-M800 proved to be effective in removing P in a wide range of pH values. This can be considered a significant advantage of these filter materials for their practical application. However, it is worth noting that WHC-M800 resulted in extremely high pH values (11-12) in the post-adsorption solutions, which may be harmful to the growth of wetland plants. Due to this undesirable side-effect, the wide application of WHC-M800 as a potential substrate in CWs should be restricted to the acidic soils, where WHC-M800 can not only adsorb P but also neutralize the medium.

3.2.2. *The effect of adsorbent dosage*

This study investigated the effects of adsorbent dosage (0.5-5.0 g/75 mL) on P removal efficiency and P adsorption capacity of WHC and WHC-M800. The data are displayed in Figs. 3c and 3d.

As can be seen from Figs. 3c and 3d, the P removal efficiencies of both WHC and WHC-M800 were proportional to the adsorbent doses. P removal efficiencies rose from 4.56% to 87.55% and from 50.52 to 99.9% for WHC and WHC-M800, respectively, when the adsorbent dose increased from 0.5 to 5.0 g/75 mL. This can be explained by the fact that more

adsorption sites were available at a higher adsorbent dose. A similar trend was reported by Patil Mansing and Raut (2013) for P capture by laterite soil. In contrast, the P adsorption capacity of WHC was found to decline from 1.12 to 0.79 mg/g when the adsorbent dose was elevated from 3 to 5 g/75 mL. The same trend occurred with WHC-M800, when its P adsorption capacity was diminished from 4.5 to 0.9 mg/g with a rise in the adsorbent dose from 0.5 to 5.0 g/75 mL. It can be explained by the fact that a higher adsorbent dose resulted in a greater number of adsorption sites on the surface of adsorbents. However, the number of phosphate anions in the solution was limited. When all phosphate anions in the solution were captured by some adsorption sites, the increment in adsorption sites as the result of the increasing adsorbent dose could not enhance the P uptake. The P adsorbed amount remained constant as the material mass rose, leading to a decline in P sorption capacity of the media (Deng and Wheatley, 2018).

3.2.3. The effect of temperature

The effects of temperature on P removal efficiency and P sorption capacity of WHC and WHC-M800 were studied using four temperatures (25, 30, 35, and 40 °C). Because of the significant difference in the P sorption capacity between WHC (raw material) and WHC-M800 (calcined material), different adsorbent doses and contact times were used in these experiments. The data are depicted in Figs. 3e and 3f.

It is clear from Figs. 3e and 3f that both P removal efficiency and P adsorption capacity of two investigated materials increased when the temperatures rose. This finding agrees with that reported by Deng and Wheatley (2018), who observed that the P adsorption capacity of the recycled concrete aggregate was enhanced at higher temperatures. Ramprasad et al. (2017) also discovered that the P removal efficiency during the summer was greater than that in other seasons. The better P removal efficiency at a higher temperature can be attributed to the formation of new active sites, leading to the augmentation of P adsorption into microspores of

the filter material (Andreo-Martínez et al., 2017). The above results suggested that the P adsorption processes of WHC and WHC-M800 had an endothermic nature.

3.2.4. The effect of contact time

Regarding the effects of contact time, there was a common trend for both WHC and WHC-M800. As is illustrated by Fig. 5, higher P removal efficiency was observed at a longer contact time until the adsorption equilibrium was reached. This is probably because as a result of longer contact time, a larger number of adsorption sites on the adsorbent surface were attached by phosphate anions in the solution. However, after reaching equilibrium, since all adsorption sites had been saturated by phosphate anions, and the extension of the contact time no longer improved P sequestration. A similar trend was reported by Patil Mansing and Raut (2013) for P sequestration by laterite soil.

With reference to the P removal rate, as shown in Fig. 5, very high P removal efficiency was achieved in a relatively short time. Specifically, for WHC, with the adsorbent dosage of 3 g/75 mL, the P removal efficiency was approximately 70% after 12 h, reaching almost 90% after 26 h. For WHC-M800, with the adsorbent dosage of 0.5 g/75 mL, the P removal percentage of WHC-M800 was above 80% only after 0.8 h, approaching 99% after 2.5 h. The substantially faster P removal rate of WHC-M800 compared to WHC can be attributed to CaO in WHC-M800, which was reported to be more effective in binding to phosphate anions than CaCO₃ in WHC (Vohla et al., 2011). The contact time needed for almost complete P elimination by both WHC and WHC-M800 was relatively short (< 2 days). This may favor their actual application as substrates in horizontal sub-surface flow constructed wetlands (HSSF-CWs), which require a hydraulic retention time (HRT) in the range of 2-5 days (Wu et al., 2015). In brief, WHC and WHC-M800 are totally appropriate as substrates in HSSF-CWs to intensify P removal in regard to the P removal rate.

3.3. Adsorption isotherm and kinetic studies

3.3.1. Adsorption isotherm study

The isotherm constants and R^2 values obtained by matching experimental data with the Langmuir and Freundlich isotherm models are shown in Table 3.

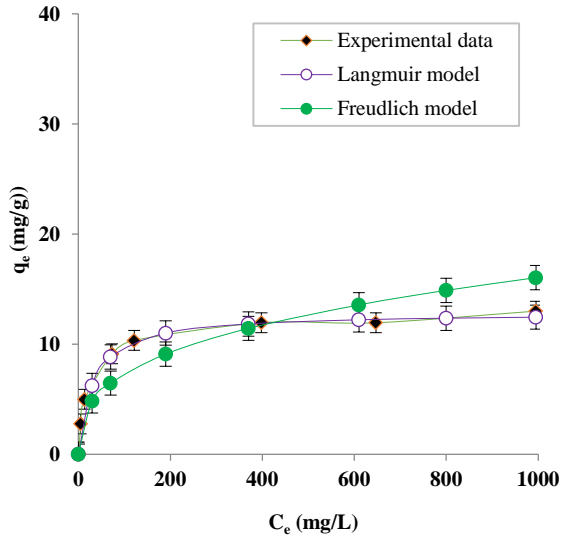
Table 3

Adsorption isotherm and kinetic characteristics of WHC and WHC-M800.

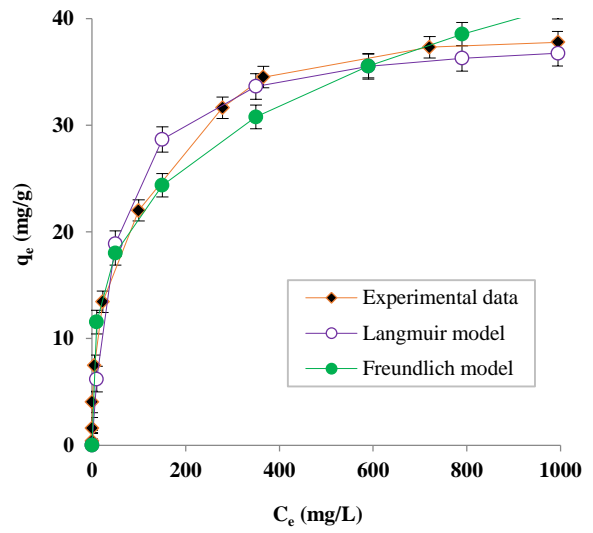
Isotherm constants and values of R^2 of WHC and WHC-M800						
Isotherm model		Langmuir		Freundlich		
Material	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(L/mg) ^{1/n}	1/n	R^2
WHC	12.8	0.03	0.997	1.5	0.344	0.88
WHC-M800	38.7	0.02	0.990	6.1	0.276	0.90

Kinetic constants and values of R^2 of WHC and WHC-M800						
Kinetic model	Pseudo- first-order model			Pseudo-second-order model		
Material	q_e (mg/g)	k_1 (1/h)	R^2	q_e (mg/g)	k_2 (g/mg/h)	R^2
WHC	2.44	0.19	0.99	2.46	0.024	0.84
WHC M800	9.55	1.98	0.99	12.02	0.104	0.91

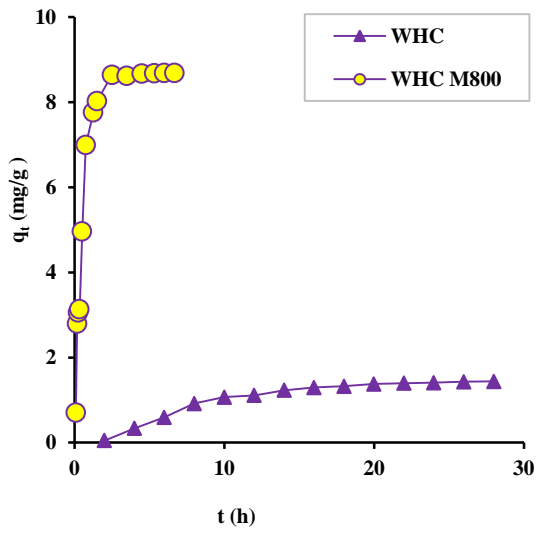
It can be seen from Table 3 that Langmuir isotherm model demonstrated higher correlation coefficients (R^2) than Freundlich isotherm models for both WHC and WHC-M800. Therefore, it can be concluded that the former was better than the latter in describing the isotherm data of WHC and WHC-M800. The obtained results showed that P retentions by WHC and WHC-M800 were characterized by monolayer adsorption. The experimental data did not match the Freundlich isotherm model due to unsatisfactory R^2 value.



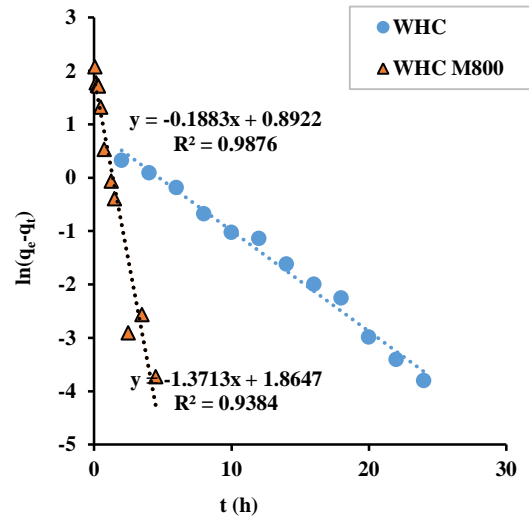
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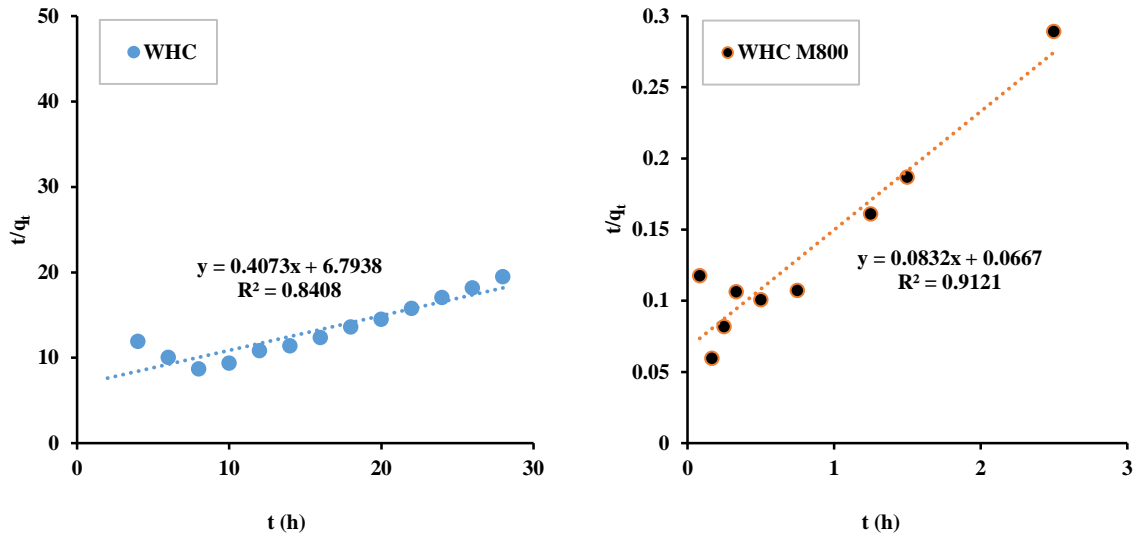
b)



c)



d)



e)

f)

Figure 4

P adsorption isotherms and kinetics of WHC and WHC-M800: a) Isotherm curve of WHC, b) Isotherm curve of WHC-M800, c) Variation of P concentrations with time, d) Data fitting by linear form of first-order kinetic model, e) Data fitting by linear form of second-order kinetic model of WHC, and f) Data fitting by linear form of second-order kinetic model of WHC-M800.

Fig. 4 reveals the P adsorption capacities of WHC and WHC-M800 under the effect of the initial P concentrations. As Fig. 4 shows, the maximum P adsorption capacity of WHC-M800 (38.7 mg/g) was almost 3 times higher than that of WHC (12.8 mg/g). Evidently, calcination markedly enhanced P retention capacity of the WHC-M800 compared to WHC. This proves that calcination is an effective method in improving P capture capacity of Ca-rich materials. However, in order to ensure the practical application of the filter material, side effects of calcination (e.g. mechanical strength of the calcined material, material weight losses during calcination and adsorption processes, extremely alkaline pH value of post-adsorption solutions etc.) should be taken into consideration when the modification methods are selected. For comparison purposes, the adsorption capacities of WHC, WHC-M800 and other filter materials are summarized in Table 4.

Table 4

Comparing the P adsorption capacity of WHC, WHC-M800 and other filter materials.

Material	P adsorption capacity (mg/g)	Reference
<i>Naturally occurring materials</i>		
Apatite	4.76	Molle et al., 2005
Dolomite	7.34-51.02	Karaca et al., 2004
Gravel	3–3.60	Vohla et al., 2005
Laterite soil	1.32	Patil Mansing and Raut, 2013
Limestone	0.3-20	Vohla et al., 2011
<i>Industrial by-product materials</i>		
Blast furnace slag	9.15	Korkusuz et al., 2007
Coal slag	1.37	Chan et al., 2008
Coal ash	0.08-29.50	Yan et al., 2007
Concrete aggregate	6.88	Deng and Wheatley, 2018
Fly ash	90.09-107.53	Lu et al., 2009
Oyster shell	0.83	Seo et al., 2005
WHC	12.80	This study
WHC-M800	38.70	This study
<i>Man-made materials</i>		
Filtralite P TM	2.50	Ádám et al., 2007
LWA	12	Vohla et al., 2011

As shown in Table 4, the maximum P adsorption capacities of WHC and WHC-M800 were 12.8 and 38.7 mg/g, respectively. These values are considerably higher than those of other seashells, such as blue-shell (0.52 mg/g), oyster shell (7.1 mg/g), and clam shell (6.65

mg/g) (Nadeem et al., 2018). They are also superior to many naturally occurring filter materials (e.g. apatite, gravel, laterite soil), industrial by-product materials (e.g. coal slag, concrete aggregate, oyster shells), or comparable to several man-made materials (e.g. Filtralite P[®], LWA). This proves that WHC and WHC-M800 are promising filter media in CWs with respect to P sequestration capacity.

3.3.2. Adsorption kinetic study

Kinetic study plays an important role in examining an adsorptive material because it not only provides useful information about the adsorption rate but also contributes to elucidating the adsorption mechanisms of the material (Nguyen, 2015). In this study, kinetic tests were conducted with the initial P concentration of 50 mg P/L and pH 7.06. The variation of adsorbed P per gram of adsorbents with time for WHC and WHC-M800 are presented in Figs. 4c. It can be seen that WHC-M800 adsorbed P much faster than WHC. The P adsorption on WHC-M800 reached equilibrium in two hours, whereas it took nearly a day for WHC.

The large difference in the P adsorption rates of WHC and WHC-M800 can be explained by (1) increasing pore size as a result of calcination, and (2) more CaO availability for P precipitation on WHC-M800. The rate constants (k) and correlation coefficients (R^2) for both the first and second order adsorption models are summarized in Table 3. R^2 values demonstrate that First-order model is better than Second-order model for modelling adsorption kinetics of both WHC and WHC M800. The k_1 value shows that WHC-M800 can adsorb P more than 10 times faster than WHC. This puts WHC-M800 at an advantage in the P retention rate when compared to WHC.

3.4. Fractionation of inorganic P

Fractionation of inorganic P in the spent filter materials plays a significant role in screening adsorptive filter media for use in CWs because it helps to elucidate the P removal mechanisms and evaluate the bioavailability of the adsorbed P.

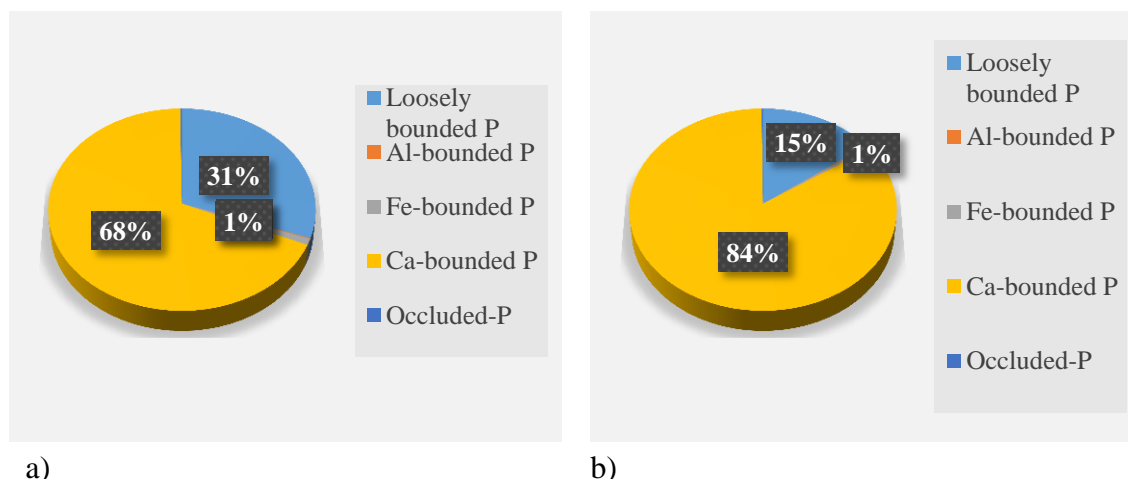


Figure 5

The percentages of inorganic P binding forms in a) WHC and b) WHC-M800.

Fig. 5 illustrates the percentages of P binding forms in WHC and WHC-M800. Fig. 5a shows that for WHC, Ca-P was the most predominant form (68.23%), followed by LBP (30.44%) > Fe-P (0.98%) > O-P (0.23%) > Al-P (0.13%). The fractionation results of P binding WHC revealed the P adsorption mechanisms by WHC involved both chemisorption (evidenced by its Ca-P percentage) and physisorption (evidenced by its LBP). Of which, the chemisorption was more prevailing than physisorption (evidenced by its higher percentage of Ca-P than that of LBP). The chemisorption was resulted from the chemical reaction of PO_4^{3-} anions in the aqueous solution and metals cations (e.g. Ca, Fe, Al) in WHC, whereas the physisorption was caused by the electrostatic interactions between negatively charged PO_4^{3-} anions in the aqueous solution and positively charged functional groups on the WHC surface. From Fig. 5b it is clear that for WHC-M800, the magnitude order of inorganic P binding forms was the same but their percentages were different from those of WHC. Specifically, the proportion of Ca-P in WHC-M800 was increased, whereas percentages of all other forms were diminished. These findings were strongly supported by XRF results of WHC and WHC-M800 (Table S3), indicating that: i) CaO was the most dominant compound (> 50%), whereas other metal oxides were the minor constituents (< 0.1%), and ii) CaO in WHC-M800 (56.38%) was more abundant than that in WHC (53.92%). Similarly, the fractionation of

Shellsand and Filtralite P[®] also showed that Ca-P was most dominant inorganic P binding form (Ádám et al., 2007). This implied that the P was removed by these two materials via the same chemisorption mechanism as the WHC and WHC-M800. According to Ádám et al. (2007) and Krogstad et al. (2005), Ca-P was more available to plants than Fe-P and Al-P. Therefore, a higher proportion of Ca-P and lower percentages of Fe-P and Al-P in WHC-M800 can be considered as a beneficial characteristic of WHC-M800. Since the percentages of Ca-P and LBP in the P adsorbed WHC and WHC-M800 are quite high, these materials can be recycled as soil amendments to supplement not only P but also Ca elements to plants. However, under certain conditions of pH and redox potential, the LBP can be transformed into tightly bound P forms as a result of complexation and precipitation (Deng and Wheatley, 2018). Therefore, it is important to control physicochemical conditions in the soil in order for the plants to receive optimal nutrition.

3.5. Efficacy of the filter media in the real wastewater

The real wastewater may contain anions that compete with PO_4^{3-} for the adsorption on WHC and WHC-M800. Consequently, the data obtained with the synthetic wastewater may lead to an overestimation of the P sequestration capacities of the filter media. For this reason, it is essential to evaluate the P decontamination efficacies of these filter materials in real wastewater. The data are depicted in Fig. 6.

As observed in Fig. 6, the P removal efficiencies of WHC and WHC-M800 in the real anaerobically digested swine wastewater fell by 10.9% and 14.4%, respectively, compared to those in the synthetic wastewater. This can be attributed to the competing effects of co-existing anions in the real wastewater. However, the P removal efficiencies of WHC and WHC-M800 were still reasonably high, indicating that the competing effects were at acceptable levels. The higher reduction in P removal efficiency of WHC-M800 can be considered a disadvantage of WHC-M800 when compared with WHC.

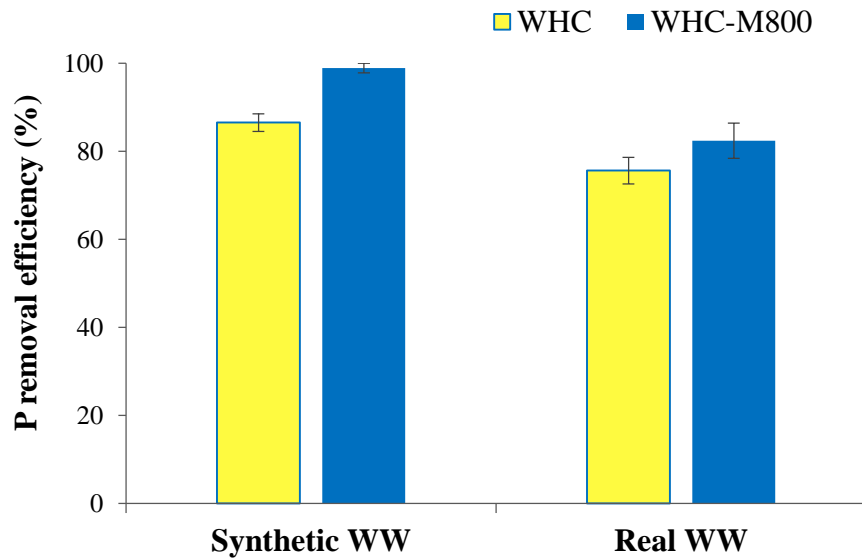


Figure 6

Comparing the P removal efficiencies of WHC and WHC-M800 in the synthetic and the real anaerobically digested swine wastewater.

3.6. Applicability of the filter materials as substrates in the constructed wetlands

In order to fulfil the potential of filter media for enhancing P removal in CWs, the candidate materials need to satisfy several selection criteria. Of these, P sorption capacity and hydraulic conductivity are the most important (See et al., 2005). Other fundamental factors need to be taken into consideration, such as local abundance, cost, durability, harmful side-effects, and recyclability of the saturated filter media (Yang et al., 2018). The present study evaluates the applicability of WHC and WHC-M800 as filter media to intensify P removal in CWs by using a simple additive scoring system, which was modified from Ballantine and Tanner (2010). The data are shown in Table 5.

Table 5

Filter media screening scores obtained with WHC and WHC-M800.

No	Evaluation Criteria	Evaluation weight	Ideal material		WHC		WHC-M800	
			Category	Score	Category	Score	Category	Score
1	P sorption capacity	3	High	9	Medium	6	High	9
2	Hydraulic conductivity	3	High	9	High	9	Medium	6
3	Mechanical strength	3	High	9	High	9	Low	3
4	Efficacy in real wastewater	2	High	6	Medium	4	Medium	4
5	P removal rate	2	High	6	Medium	4	High	6
6	Reuse potential after saturation	2	High	6	High	6	Low	2
7	Toxic side-effect	2	Low	6	Low	6	High	2
8	Energy consumption	2	Low	6	Low	6	High	2
9	Availability in Vietnam	1	High	3	High	3	Low	1
10	Likely cost	1	Low	3	Low	3	High	1
CUMULATIVE SCORE			0/9*	63	0/7*	56	6/2*	36

Notation:

For beneficial criteria (1, 2, 3, 4, 5, 6, 9): High = 3 scores, Medium = 2 scores, Low = 1 score

For harmful criteria (7, 8, 10): Low = 3 scores, Medium = 2 scores, High = 1 score

Criteria with 3 scores = Advantages; Criteria with 1 score = Disadvantages; * = Disadvantage/Advantage ratio.

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As indicated in Table 5, WHC-M800 was characterized by two advantages and six disadvantages. These advantages included a superior P retention capacity (38.7 mg/g) and an extremely fast P removal rate (99% after 2.5 h). However, WHC-M800 also demonstrated several demerits. To begin with, it had a poor mechanical strength. This was evidenced by the observation of adsorption tests with WHC-M800. There was a layer of white precipitate at the bottom of all flasks at the end of the test. This can be explained that WHC-M800 with high content of CaO could absorb water vapor to form $\text{Ca}(\text{OH})_2$. This compound was reported to be slightly soluble in the water, being 1730 mg/L at 20 °C (Shiu et al., 1990). This assumption was strongly supported by the fact that the weight loss of WHC-M800 after adsorption was very high, being up to 25%. The poor mechanical strength leads to the need of replacing filter materials more often, thus this was considered as an undesirable property of the WHC-M800. Regarding undesirable side-effects, WHC-M800 resulted in extremely high pH values in the post-adsorption solutions (~12) as a result of $\text{Ca}(\text{OH})_2$ generation. Consequently, the P saturated WHC-M800 did not have much reuse potential as a soil amendment. Another harmful side-effect was high weight loss during calcination (14%), which can be attributed to water evaporation, burning of residual organic matter, and decomposition of CaCO_3 into CaO (Ngo et al., 2017). As a result, a larger amount of raw WHC and energy was required to yield the same quantity of WHC-M800. A greater weight loss (> 40%) was reported by Ngo et al. (2017) for calcination of cockle shells. This was probably due to a higher calcination temperature (930 °C) utilized in that study. More important was the fabrication of WHC-M800 consumed a lot of energy, thereby increasing the GHGs emissions and accelerating global warming. In addition, the cost of WHC-M800 was relatively high due to intensive energy consumption for WHC calcination. This may hinder the practical application of WHC-M800 since CWs are known as a low-cost technology (Yang et al., 2018). Finally, as a man-made material, WHC-M800 was not abundantly available in Vietnam.

In contrast, WHC demonstrated no disadvantages but seven advantages instead. It is interesting to note that two advantages belonged to the group of critical criteria, these being excellent hydraulic conductivity (0.8 cm/s) and high mechanical strength. The latter property of WHC can be attributed by the main composition of WHC was CaCO_3 , which had very low solubility in water (Shiu et al., 1990). This agreed well with the minor weight loss of WHC after adsorption test, being only 0.3%. In addition, it exhibited negligible harmful side-effect, evidenced by near neutral pH values in the post-adsorption solutions (7.38). Because there were no toxic effects, the P-saturated WHC can be potentially recycled as a P-rich soil amendment. Furthermore, WHC can be found easily in a large amount (> 300,000 ton/year) as the waste/by-product of the marine culture and seafood processing industry in Vietnam. Moreover, the processing of WHC did not require high energy use, hence it made a substantial contribution to mitigating climate change. As a consequence, WHC was very cheap or even free of charge in Vietnam. In addition to the above advantages, WHC exhibited a reasonably high P capture capacity (12.8 mg/g), reasonably high efficacy in real wastewater (75.6%), and applicable P removal rate (90% after 26 h).

It is clear from Table 5 that the cumulative score of WHC (56) was closer to that of the ideal filter material (63) and significantly higher than that of WHC-M800 (36). Also the disadvantage/advantage ratio of WHC and WHC-M800 was below 1 and equal to 3, respectively. The results indicated that WHC had a greater potential as a filter media for intensifying P elimination in CWs than WHC-M800. The recycling of WHC for this purpose is expected to enhance the P-rich wastewater purification, prevent odor pollution, and reduce waste WHC disposal in a simple, cheap, and eco-friendly way. Hence, it contributes to a sustainable agriculture development in Vietnam.

Despite the significant advantages of WHC, some challenges may occur associated with up-scaling the WHC-based CWs to the real situation. Firstly, as the wetland substrate, WHC needs to be collected with a huge quantity, thus leading to high cost of WHC collection.

Secondly, the sites of CWs may be far from the seafood processing factories, coastal areas, etc., resulting in high cost of WHC transportation. Thirdly, the large-scale gridding of WHC requires specialized industrial crushers and consumes a lot of energy. Finally, WHC in CWs will be saturated after a certain period of operation, hereby requiring the regeneration of WHC or replacing the saturated WHC with the new WHC. To solve these problems, the WHC-based CWs are highly recommended for coastal areas, where WHC supply source is abundant. In addition, the heat recovered from solid waste incinerators or renewable energy can be utilized for WHC grinding instead of the fossil fuel. Furthermore, P solubilizing bacteria can be applied to the saturated WHC-based CWs to turn non-dissolved P adsorbed on WHC into the bio-available P form, which can be easily uptaken by wetland plants. By that way the P content in the saturated WHC will be diminished and approached the P content in the pristine WHC. The recovered WHC-based CWs can be then continued to use for the treatment of P-rich wastewater.

4. Conclusion

In this study, WHC and WHC-M800 was explored as the wetland filter media for P decontamination. WHC-M800 exhibited a substantially higher q_{\max} value (38.7 mg/g) than WHC (12.8 mg/g), suggesting that calcination was an appropriate method to intensify the P sorption capacity of Ca-rich materials. The P sorption by both WHC and WHC-M800 had the endothermic nature and followed the Langmuir isotherm and Pseudo-first-order kinetic models. The P removal pathway of WHC and WHC-M800 was mainly via chemical sorption in the form of Ca-P binding. While WHC was proven to be a promising wetland filter media, the actual use of WHC-M800 for this purpose can be restricted due to significant drawbacks. Future works on the practical application of WHC in the real CWs are recommended to focus on: i) optimization of operating conditions, ii) clarifying the P removal mechanisms, iii)

estimation of the lifespan of WHC-based CWs, and iv) regeneration of P-bearing WHC after saturation.

Acknowledgments

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