Hybrid use of coal slag and calcined ferralsol as wetland substrate for improving phosphorus removal from wastewater

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Abstract

In this study, natural ferralsol (NF) was calcined to enhance its phosphorus (P) adsorption. The NF and calcined ferralsol at the selected temperature (CF500) were characterized by SEM, FTIR, XRD, XRF and other experiments to elucidate changes in morphology and physicochemical properties. CF500 and coal slag (CS) were examined as wetland media individually and combinedly. The applicability of CF500 and CS as the hybrid media in the lab–scale horizontal sub–surface flow constructed wetlands (HSSF–CWs) was evaluated. It was found that 500 ^{o}C was the best calcination temperature of NF for P adsorption. The maximum P adsorption capacity of CF500 (19.4 mg/g) was 60.4 ± 2.2 % greater than that of NF. While isotherm data of P sorption by CF500 were fitted both Langmuir and Freundlich models, the kinetic data was better described by Pseudo-second-order model. Thermodynamic parameters revealed the endothermic and spontaneous nature of the P sorption by CF500. The combination of CF500 and CS leveraged the merits of individual substrates while mitigated their demerits. The optimal mixing ratio of CF500 to CS was 1.25:1 by volume. The hybrid CF500–CS substrate HSSF–CWs demonstrated satisfactory P removal efficiency (99.44% ± 0.1) and effluent P concentration (0.08 ± 0.01 mg/L). Application of the mixed substrate in the HSSF–CWs resulted in negligible side effects on their effluent quality. Due to abundant availability of raw materials, simplicity of preparation, as well as efficiency and safety of application, a mixture of CF500 and CS is a promising hybrid substrate in HSSF–CWs for P–rich wastewater decontamination.

Keywords: Calcined ferralsol; coal slag; hybrid substrate; constructed wetlands; phosphorus adsorption; P–rich wastewater

1. Introduction

It is well–known that excessive amounts of phosphorus (P) cause eutrophication in the water medium, which is harmful to the aquatic and human life and ecosystems generally [1]. To date, numerous methods have been applied in P–rich wastewater decontamination, such as chemical precipitation [2], activated sludge e.g. models of Bardenpho [3], Phoredox [4], modified University of Cape Town [5], adsorption [1], and constructed wetlands (CWs) [6]. Of these, CWs are emerging as a 'green', reliable, affordable and versatile technology, which is potentially helpful for developing countries and especially in small and medium–sized rural communities [7]. While CWs can successfully remove organic matters, total suspended solid (TSS), and nitrogen (N), they are found to be less efficient in removing P. The P removal efficiency of all categories of CWs is usually limited to only 40-60% unless adsorptive substrates are selected [8]. This can sometimes be a bottleneck, limiting the wide application of CWs in real–life scenarios. For this reason, it is essential to enhance the P treatment performance of CWs.

It has been well established that substrates are of great significance in removing P. While substrate capture contributes 36.2–87.5% of phosphorus removal, plant and microbial uptake represents 1.3–26.4% [6]. Since the conventional substrates (e.g. gravel, stone) usually possess limited P sorption capacity, there is an increasing trend to use raw and modified adsorptive materials (e.g. magnesia, steel slag, sponge iron) as wetland substrates [6]. It is reported that the P adsorption by CWs can be largely enhanced by substrate modification. The removal of P from the decentralized rural sewage in the modified zeolite baffled flow constructed wetland (BFCW) in Suzhou City was investigated. It was revealed that the modified zeolite wetland exhibited a high and stable P removal, which was 1–time higher than that of the zeolite wetland [9]. Chemical modification of wetland substrates, which is usually conducted with acid, alkali, and inorganic salts, has certain disadvantages such as high cost and secondary pollution. Conversely, physical modification of wetland substrates, which has merits of being cheap and environmentally safe, are rarely applied [10].

Recently, there has been a growing trend in using hybrid substrate CWs for wastewater treatment. That is because composite substrates can: (i) improve pollutant removal, (ii) reduce side effects (e.g. high pH values in the effluent), and (iii) promote simultaneous removal of contaminants, e.g. COD_{Cr}, NH_4^+–N, total nitrogen (TN), soluble reactive phosphorus (SRP), and total phosphorus (TP) [11]. Unfortunately, most studies on the combined substrates focus on the removal of N and other pollutants rather than P. It was reported that gravel–slag–wood chip combined with substrate baffled subsurface–flow constructed wetlands (BFCWs) exhibited high satisfactory removals of COD (97%), NH_4^+–N (95%), and TN (94%) [12]. In another study, 48.2–61.2% COD, 93.5–99% N, and 90% heavy metals were eliminated from rural landfill leachate using horizontal sub–surface flow constructed wetlands (HSSF–CWs), which were packed with zeolite–slag hybrid substrate [13]. Until now, very few studies are available on the utilization of composite substrates to strengthen P removal [10]. It was found that a relatively high P removal efficiency (83%) from fish processing wastewater and low P concentration in the effluent (0.5 mg/L) occurred when applying the mixture of basaltic soil and acidic soil (80:20 by weight ratio) in the filter system [14]. This was attributed to the high P binding capacity of basaltic soil and good adhesion ability of acidic soil, which favored the shaping of filter materials, and thus improving the circulation of wastewater in the filtration system. It was indicated that the HSSF–CW using hybrid adsorptive media of zeolite, vermiculite and vesuvianite brought about 86.5% TSS, 68.1% COD, 78.25% TN, 95.2% NH_4^+ and 64.85% TP from highway runoff [15]. It is reported that pumice-amended mixture was better than zeolite-amended one in improving P removal from wastewater [16]. It can be seen that adsorptive materials are usually selected as the components of composite substrates to enhance P treatment performance of CWs. In order to avoid water clogging in CWs, non–adsorptive materials (e.g. slag, wood chips, and acidic soils) are often employed. For this purpose, the utilization of waste–derived materials (e.g. slag, construction materials) has received much more attention in recent years [12,13]. This not only helps minimize the cost of wetland construction but also diminish the environmental burden caused by solid waste disposal [10].

Although using hybrid substrates has many advantages, there is still insufficient information on the use of hybrid substrate HSSF–CWs, which combine industrial by–products and locally available, physically modified, adsorptive materials to augment P removal from wastewater. Thus, in this study, coal slag (CS) and calcined ferralsol at 500 ^{o}C (CF500) were employed as the composite substrate in lab–scale HSSF–CWs planted with water spinach *(Aquatica ipomoea)* and lemongrass *(Cymbopogon citratus)*. The objectives of this work were to: (i) investigate the possibility of modifying natural ferralsol (NF) by calcination to enhance its P retention; (ii) evaluate potential of hybrid use of CF500 and CS as wetland substrates; and (iii) explore the applicability of the CF500–CS mixed substrate lab–scale HSSF–CWs in the removal of P from aqueous solutions. To the best of the authors's knowledge, this is the first time the hybrid CF500–CS substrate HSSF–CWs have been investigated for P–rich wastewater decontamination. This study is expected to pave the way for recycling of CS, an industrial by–product of thermal power plants, for environmental treatment purpose, thereby aiming at the dual environmental benefits. In addition, the use of CF500, an adsorptive filter material, as the wetland media is predicted to strengthen the P removal efficacy of HSSF–CWs, thus enabling their wider practical application.

2. Materials and methods

2.1. Materials

In this study, CS was selected as the supporting material in CWs because it has high porosity [17,18], thereby preventing water clogging in CWs and large amounts of Fe, Al, and Ca, suggesting high potential for P sorption. Recycling of CS, an industrial by–product, in wastewater treatment helps reduce its environmental concern. CS was collected from Pha Lai Thermal Power Joint Stock Company in Chi Linh district, Hai Duong province, Vietnam. On the site, the large CS particles were removed by using a big steel sieve with square holes of 6 mm x 6 mm. Then, in the lab, particle size distribution of CS was examined. The result showed that CS particles of 1.4–5.6 mm accounted for 69% of the total weight, and were selected to use as the substrate in HSSF–CWs. The removal of large (> 5.6 mm) and fine CS particles (< 1.4 mm), which presented less than 30%, ensures the uniformity of the wetland substrate bed while avoids water clogging probably caused by fine particles. With the selected particle size range of CS, the overall porosity of the CS bed was 57.0 ± 0.3%. NF was collected at Thuan Hanh T–junction, Dak Song district, Dak Nong province, Vietnam. NF was selected as a raw substrate because it is abundant throughout the world (750 million ha) and in Vietnam (accounting for 65.2% of the whole territory) [19]. Additionally, it has abundant iron (Fe) and aluminum (Al), which may enhance P removal [20]. First, NF was collected from the soil layer of 0.5 m below the soil surface to avoid the effects of agricultural activities. Then, it was transported to the Laboratory of the Master's Program in Environmental Engineering (MEE), Vietnam Japan University – Vietnam National University, Hanoi (VNU–VJU) for temporary storage. Next, calcination of NF at lab–scale and large–scale was carried out to produce CF500. After that, CS and CF500 were utilized for adsorption tests. Finally, the mixture of CF500 (< 2.8 mm) and CS (1.4–5.6 mm) was applied as the hybrid substrates in the HSSF–CWs (E–Supplement figure, Fig. S1). While the very high porosity of CS can help to prevent water clogging, abundant metal oxide contents of ferralsol are expected to enhance P retention. Furthermore, water spinach *(A. ipomoea)* and lemongrass *(C. citratus)* were selected as wetland plants because they are ubiquitous in Vietnam, highly tolerant to flooding and P, easy to cultivate, grow fast, accumulate a lot of P (0.95% and 0.089% by dry weight for *A. ipomoea* and *C. citratus*, respectively) [21,22] and are economic crops.

The synthetic wastewater, which simulated the composition of 4–fold diluted anaerobically digested swine wastewater samples in terms of ortho phosphate (~12.5 mg P/L) and ammonium (~125 mg N/L) was prepared by dissolving specific amounts of KH_2PO_4 and

NH_4Cl in tap water. Though this study aims to eliminate only ortho phosphate, ammonium was added to the synthetic wastewater to support plant growth. Bench experiments were conducted to modify and characterize the selected substrates. After that, the lab–scale hybrid substrate based HF–CWs were set up to evaluate the extent of P removal from aqueous solutions.

2.2. Calcination of natural ferralsol for enhancing its phosphorus adsorption

2.2.1. Selection of calcination temperature

The NF was calcined to enhance their P sorption capacity. To begin with, NF was thermally treated for 2 h at the lab–scale. Three temperatures (300, 500, and 700 ^{o}C) were tested using the furnace (CWF12/13, Carbolite, England). The optimal calcination temperature was determined based on the P sorption capacities of the calcined ferralsols and the pH values of the post–adsorption solutions. In the next step, the calcination of NF was conducted at a large–scale setting with the selected calcination temperature in Bat Trang pottery village, Gia Lam district, Hanoi. The NF was loaded on 5 different trays (L x W x H = 180 cm x 45 cm x 10 cm) inside a commercial furnace, where the inside temperature was controlled automatically with a sensor controller. It took 6 hours to reach the selected calcination temperature, followed by 2 hours for calcination of NF at the constant temperature. Then, the commercial furnace was turned off and cooled down till it reached ambient temperature. Finally, the calcined ferralsol were packed and transported to the laboratory for further investigation. The lab–scale and large–scale calcined ferralsols were tested for comparison of their P sorption abilities.

2.2.2. Characterization of natural ferralsol and calcined ferralsol

Characterization analyses (SEM, XRD, XRF, and FTIR) were done with NF and CF500 to clarify the effects of calcination on their morphology, structure, composition, and functional groups, which were closely related to their P sorption capacities. SEM images were acquired using scanning electron microscope (JSM–IT100, Jeol, Japan). XRD and XRF measurements were implemented using X–ray diffractometer (Empyrean, PANalytical, Netherlands) and WDXRF spectrometer (S4 Pioneer, BrukerE AXS, Germany), respectively. FTIR analyses were performed using FTIR Spectrometer (FT/IR–4600typeA, Jasco, Germany).

2.3. Properties of filter materials

2.3.1. Physicochemical properties

Porosity of a filter material is the ratio of the volume of void space to the total volume of the material, which is estimated using the Eq. (1) as follows [23]:

$$\text{Porosity} = \frac{\text{Volume of voids}}{\text{Total volume}} \text{ x } 100\% \qquad (1)$$

Hydraulic conductivity measures the ability of the material to transmit fluid through pore spaces and fractures in the presence of an applied hydraulic gradient. Darcy's Law defines the hydraulic conductivity as the ratio of the average velocity of a fluid through a cross–sectional area (Darcy's velocity) due to the applied hydraulic gradient. The hydraulic conductivity of a filter material is calculated by the following Eq. (2) [23]:

$$K = \frac{Q * L}{A\,(H_1 - H_2)} \qquad (2)$$

Where K is hydraulic conductivity (cm/s), Q is volumetric flow rate (cm^3/s), L is the height of material layer (cm), A is cross–sectional area (cm^2), and $H_1 - H_2$ represents a difference in hydraulic heads (cm).

In this study, hydraulic conductivity was measured for both single substrates (CF500 and CS) and hybrid substrates (CF500 and CS) with various mixing ratios (1:1, 1.25:1; and 1.5:1 by volume). The texture and density of single substrates (CF500 and CS) were analyzed according to the TCVN 8567:2010 and TCVN 11399:2016 methods, respectively.

The chemical properties ($pH_{H2O,}$ organic matter, total P, available P, $Fe_{oxalate,}$ and $Al_{oxalate}$) of filter materials (CF500 and CS) were analyzed by employing the respective analysis methods of TCVN 5979:2007, TCVN 8941:2011, TCVN 8941:2011, TCVN 5256:2009, and Fe, Al exchangable oxalate extraction.

2.3.2. Adsorptive properties

The batch adsorption tests were implemented to compare adsorptive behaviors of NF and calcined ferralsols, which were obtained at different calcination temperatures (300, 500, and 700 ^{o}C). The tests also served to evaluate the adsorptive properties of the potential wetland substrates (CF500, CS), which included kinetics, isotherms, and thermodynamics. The specific conditions for batch adsorption tests are presented in Table 1.

Table 1

2.4. Lab–scale HSSF–CW units

2.4.1. Configurations

The lab–scale horizontal sub–surface flow constructed wetlands (HSSF–CWs were set up in a planting house, in Cau Giay, Hanoi, Vietnam. This building had a transparent roof to receive the sunlight while avoiding rainwater. Four HSSF–CWs units in parallel were arranged near a storage tank. Each HSSF–CW was made of stainless steel (inox 340) with the following dimensions (L x W x H = 68.5 cm x 33 cm x 42 cm). In all 4 HSSF–CWs, stones (∅= 10–20 mm) were placed in a bottom layer (3 cm thick) to prevent water clogging, whereas yellow sand was filled up in the top layer (3 cm thick) to support the growth of wetland plants. In the middle layer (31 cm thick), while HSSF–CW1 was solely packed with CS, three remaining HSSF–CWs were filled with hybrid substrates of CS and calcined ferralsol (CF500) with the selected mixing ratio of 1.25:1 by volume. The gap (5 cm) between the sand layer and the tank surface served to prevent water overflow and substrate loss. The HSSF–CW1 and HSSF–CW2 were planted with water spinach *(A. ipomoea)* with a density of about 350 plants/ m^{2}. Using the same hybrid substrate as HSSF–CW2, HSSF–CW4 was vegetated with lemongrass *(C. citratus)* with a density of about 100 plants/ m^{2}, whereas HSSF–CW3 was un–vegetated and used as the control sample for HSSF–CWs 2&4.

2.4.2. Operating conditions

The synthetic wastewater was stored in a plastic tank (200 L) before entering the lab–scale HSSF–CWs system. It was fed into all HSSF–CWs in the horizontal flow direction using peristaltic pumps (HV–77200–50, Masterflex Cole–Parmer, USA) to ensure the same hydraulic retention time (HRT) of 5.4 days with the volumetric flow rate (Q) in the HSSF–CW1 and HSSF–CW2, HSSF–CW3, HSSF–CW4 were 8.5 and 8.0 L/d, respectively. The start–up period lasted for about half month for plant acclimation. After that, the HSSF–CWs were operated consecutively for 120 days, from March to July 2020. The setting up of the inlet and outlet of the HSSF–CWs is illustrated in E–Supplement figure (Fig. S2). The influent was pumped and distributed on the sand surface via perforated silicone tubes. At the bottom, treated wastewater was collected by perforated Ø =21 PVC plastic tubes, which were installed at other side of the tanks (1.5 cm above the tank bottom). Outlet ports were lifted to the sand surface to ensure the stable level of water in the tanks. This design was to prevent the formation of a short-circuit flow in the bottom of HSSF–CWs. The effluents of HSSF–CWs were sampled every 3 days for determining pH, electrical conductivity (EC), and P concentration.

2.5. Aqueous solution quality analysis

This work concentrated on analysis of the P levels in wastewater to evaluate the P capture ability of filter materials and HSSF–CWs. In an attempt to elucidate the possible side effects of these substrates on the quality of effluents from HSSF–CWs, some other environmental parameters (e.g. pH, EC, and heavy metal concentrations) were also measured.

The concentrations of ortho–P in aqueous solutions were measured according to Method 365.3 of the United States Environmental Protection Agency (EPA): Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Two Reagent) [24] using UV/Vis Diode Array Spectrophotometer (S2100 UV, Unico, USA) at the wavelength number of 710 nm. The pH values were monitored with SevenCompact pH/Ion meter (S220–Kit, Mettler Toledo, China).

The EC values were measured using Sension+EC5 Portable Conductivity/TDS Meter (Sension+EC5, Hach, China). The contents of heavy metals were determined employing an Atomic Absorption Spectrophotometer (ZA–3000, Hitachi, Japan). The agitation in batch adsorption tests were done with the orbital shaker (OS–3000, Jeiotech, South Korea).

2.6. Calculation and statistical analysis

2.6.1. P removal efficiency

The P removal efficiency (R_E) of an adsorbent is calculated from Eq. (3) as follows [1]:

$$R_E\ (\%) = \frac{(C_i - C_e)}{C_i}\ x\ 100\% \qquad (3)$$

where R_E is the P removal efficiency (%), C_i is the initial P concentration (mg/L) and C_e represents the equilibrium P concentration (mg/L).

2.6.2. P adsorption capacity

The P adsorption capacity of an adsorbent is calculated by the Eq. (4) as follows [1]:

$$q_e = \frac{C_i - C_e}{m}\ x\ V \qquad (4)$$

where q_e is adsorption capacity at the equilibrium (mg/g), C_i is initial P concentration (mg/L), C_e stands for equilibrium P concentration (mg/L), m is mass of the adsorbent (g), and V is volume of the adsorption solution (L)

2.6.3. Kinetic, isotherm, and thermodynamic parameters

Kinetic parameters for P sorption on CS and CF500 were determined using Pseudo first–order and Pseudo second–order kinetic models, which were determined using Eq. (5) and Eq. (6) [1]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where q_e and q_t are amounts of adsorbed phosphate per 1 gram of adsorbent at equilibrium and time t; k_1 and k_2 are the first and second rate constants. These parameters were derived from experimental data by non–linear fitting process using excel solver.

The adsorption isotherms were investigated using Langmuir and Freundlich models as expressed by following linearized forms [25]:

$$\frac{1}{q_e} = \frac{1}{q_e K_L}\frac{1}{C_e} + \frac{1}{q_e} \tag{7}$$

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e) \tag{8}$$

where q_e is equilibrium adsorption capacity (mg/g), C_e is aqueous phosphate concentration at equilibrium, K_L, K_F, n are constants. These parameters are obtained from the slope and the intercept with vertical axis of plots $1/q_e - 1/C_e$ and $\ln(q_e) - \ln(C_e)$.

Thermodynamic study of P adsorption was investigated in the temperature range of 30 ÷ 50 ^{o}C. Equilibrium constant (K_d) was determined from intercept of the plot q_e/C_e versus q_e. Then, the change in Gibbs free energy (ΔG) and other thermodynamic parameters (ΔH, ΔS) were determined with assumption that ΔH and ΔS are constant by using the following equations [25]:

$$\Delta G = -RT.\ \ln(K_L) \tag{9}$$

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

2.6.4. Statistical analysis

All lab–scale experiments were triplicated. The experimental data were statistically analyzed using Statistical Package for the Social Sciences (SPSS) 22 package. The tests for goodness of fit to a normal distribution were implemented with all data. One–way ANOVA or Independent Sample T–test was employed to compare the data, which included multiple or two variances, respectively. While $p < 0.05$ represents for statistical significance, $p < 0.001$ indicates high level of statistical significance [6].

3. Results and discussion

3.1. Calcination of natural ferralsol for enhancing its P adsorption

3.1.1. Selection of the best calcination temperature

The substrate plays a key role in removing P from constructed wetlands. To intensify the P sorption capacity of substrates, numerous modification methods were devised and applied. Of these, calcination has many advantages such as simple operation, high efficacy, limited chemical use, no secondary pollution, etc. This study investigates the possibility of improving P sorption capacity of NF by calcination and determines the best calcination temperature.

(i) Lab–scale calcination

NF was calcined at three different temperatures (300, 500, and 700 °C). CF300, CF500, and CF700 were compared with respects to P sorption capacity and post–adsorption pH value. It was found that the P adsorption capacities of CF300 (3.83 ± 0.02 mg/g), CF500 (4.68 ± 0.01 mg/g), and CF700 (4.25 ± 0.01 mg/g) were significantly different *($p < 0.001$).* Similarly, it is evident from the statistical analysis that there was significant difference in the P adsorption capacity of CF500 (4.68 ± 0.01 mg/g) and NF (2.58 ± 0.03 mg/g) *($p < 0.001$).* This strongly suggests that calcination was an effective method to augment P retention ability of NF. The higher P sorption capacity was attained with rising calcination temperature in the 300–500 °C range. This can be attributed to the larger pore size of CF500 as compared to NF. However, an increment in calcination temperature from 500 to 700 °C led to a decline in P sorption capacity. This is probable due to the collapse of pore walls at 700 °C [26]. Among three investigated calcination temperatures, 500 °C was the best with the respect to P sorption capacities of the calcined ferralsols and the pH values of the post–adsorption solutions. As a result of calcination, the maximum adsorption capacity of CF500 (19.4 mg/g) was increased by 60.4 ± 2.2 % as compared to that of NF (12.1 mg/g). Similarly, it was reported that, the P sorption ability of mussel shell after calcination at 550 °C was enhanced by 112.59% [27].

The pH values of post–adsorption solutions attained with CF300, CF500, CF700 (6.67–6.95) were higher than that of NF (6.05). While NF resulted in a slightly acidic pH value (6.05), CF300, CF500, and CF700 produced near neutral pH values (6.67–6.95). This indicates that calcination was not only efficient in enhancing P sorption capacity of NF but also enabled the neutral medium after adsorption. The most neutral pH value (6.95) was attained with CF500, suggesting that 500 °C was the best calcination temperature in terms of the pH of post–adsorption solutions. Taking both these criteria into consideration, 500 °C was selected as the best possible calcination temperature.

(ii) Large–scale calcination

In order to evaluate the possibility of producing CF500 in a large–scale scenario, the calcination of NF was conducted with a commercial furnace in Bat Trang pottery village, Gia Lam district, Hanoi, using the selected calcination temperature (500 °C) at the lab–scale. Then, two categories of CF500, which were produced at the lab–scale and large–scale, were tested for comparison purposes. Results showed that the difference in the P adsorption capacity of CF500 produced at the lab–scale (4.68 ± 0.01 mg/g) and the large–scale (4.58 ± 0.1 mg/g) was minor. This means that CF500 produced at the large–scale has the same quality as that prepared at the lab–scale. This favors the application of CF500 in the actual constructed wetlands.

3.1.2. Physicochemical properties of natural ferralsol and calcined ferralsol

It is reported that some physicochemical properties of filter materials can affect their functions as wetland substrates [28]. Among them, the most important factors, which affect the P removal of CWs, include porosity, organic matter, total P percentage, bioavailable P content, Fe & Al oxalate contents, pH of post-adsorption solution [8]. It was found that the calcination of NF resulted in rising porosity, Fe & Al oxalate contents, and pH of post–adsorption solutions. However, there was a decrease in the percentages of organic matter and total P as well as bio–available P content of NF in comparison with CF500. All these changes were observed to favor P retention by CF500. To begin with, the percentage of total organic matter in CF500 (< 0.08%) was smaller than that in NF (0.64 ± 0.03%). That is because under high temperature, some organic matters were converted into CO_2 and H_2O vaporing into the air. Due to the lower percentage of organic matter in CF500, less Fe & Al ions interact with organic matters. It means that more Fe & Al ions are available for P retention. Similarly, the bio–available P content in CF500 (0.850 ± 0.02 mg P_2O_5/100 g material) was found to be 4–fold less than that in NF (3.46 ± 0.03 mg P_2O_5/100 g material). The bio–available P is easily fixed by Fe & Al in the material, especially in acidic medium [17]. As a result, less Fe & Al were used to immobilize P or more Fe & Al were available for P sorption.

In contrast, the contents of $Fe_{oxalate}$ and $Al_{oxalate}$ in CF500 (2.28 ± 0.11 and 2.12 ± 0.06 mg/g) were 3–fold higher than those in NF, respectively (0.725 ± 0.005 and 0.851 ± 0.004 mg/g). This can be explained by the fact that, as the result of converting organic matter into CO_2, the total quantity of CF500 fell when compared to NF. Since the weights of Fe & Al in the materials were unchanged, the percentages of $Fe_{oxalate}$ and $Al_{oxalate}$ will be increased. Consequently, more P can be captured by CF500 due to higher $Fe_{oxalate}$ & $Al_{oxalate}$. Additionally, the post–adsorption solution pH of CF500 (6.18 ± 0.12) was more neutral than that of NF (5.14). The porosity of CF500 (51.3 ± 0.6%) was substantially greater than that of NF (47.7 ± 0.6%), thus preventing the water clogging once CF500 was used as the wetland substrate. For all the reasons mentioned above, it can be concluded that calcination was effective in changing the physicochemical properties of NF in the direction that enabled its P sorption.

3.1.3. Characterization of natural ferralsol and calcined ferralsol

To clarify the changes in NF after calcination, which is necessary for elucidating the P sorption capacity of the filter materials, the SEM, XRD, XRF and FTIR analyses were implemented for both NF and CF500. SEM images of NF and CF500 are shown in E–supplement figure (Fig. S3). It can be seen that the NF surface was characterized with a dense, non–porous structure while the surface of CF500 was full of pores with substantially larger diameters. This change in the morphology of CF500 agrees well with its better P sorption (4.68 ± 0.01 mg/g) as compared to NF (2.58 ± 0.03 mg/g).

XRD analysis results of NF and CF500 showed that there was a clear difference in the mineral composition between NF and CF500 (Fig. 1). Specifically, NF consisted of four minerals, whereas only three minerals could be found in CF500. The percentage of goethite fell slightly from 8% in NF to 6% in CF500. In the same trend, gibbsite, which accounted for the highest percentage in NF (50%), completely disappeared in CF500 (0%). Conversely, the percentages of kaolinite and hematite both increased by 44% and 8%, respectively. Taking P sorption capacities of NF (2.58 ± 0.03 mg/g) and CF500 (4.68 ± 0.01 mg/g) into consideration, it can be concluded that kaolinite and hematite played major roles in improving CF500's P capture ability.

Figure 1

XRF analyses were conducted to evaluate the presence of metal oxides in NF and CF500. The results are given in Table 2. It can be seen that CF500 demonstrated higher percentages of Al_2O_3, Fe_2O_3, and TiO_2 as compared to NF. As stated earlier, at the same adsorption condition, CF500 exhibited greater P sorption capacity (4.68 ± 0.01 mg/g) than NF (2.58 ± 0.03 mg/g). This suggests that the contents of these metal oxides in a filter material are proportional to its P sorption ability. Similarly, Wang et al. (2018) reported that more metal oxides favored the filter materials' ability to sorb P [10].

Table 2

FTIR analysis was done to clarify the changes in the composition of functional groups on the surface of NF and CF500 as a result of calcination. The FTIR spectra of NF and CF500 are displayed in E–Supplement figure (Fig. S4). It is observed that both NF and CF500 were dominated by peaks at the positions of 3418 cm^{-1}, 3341 cm^{-1}, 727 cm^{-1}, 658 cm^{-1}, and 535 cm^{-1}. However, in the spectrum of CF500, the peaks at position of 3244 cm^{-1}, 3157 cm^{-1}, and 411

cm^{-1} disappeared. These peaks were attributed to the functional group of OH^- of gibbsite and organic matters in materials. The decline in the number of OH^- groups can lead to much less repulsion force between PO_4^{3-} anions in the aqueous solution and the negatively charged binding sites on the surface of CF500. As a consequence, the P retention on CF500 (4.68 ± 0.01 mg/g) was enhanced as compared to NF (2.58 ± 0.03 mg/g). This finding is in line with the XRD result, which confirmed the disappearance of the gibbsite in CF500.

3.2. Physicochemical and adsorptive properties of CS and CF500

3.2.1. Adsorptive properties

This section of the paper explores the adsorptive properties of CS and CF500, including kinetic, isotherm, and thermodynamic parameters.

Kinetic analysis provides information about adsorption rate and mechanisms. Kinetic parameters of CS and CF500 are presented in Table 3. It is clear that the adsorption rate of CF500 ($k_1 = 0.247$, $k_2 = 0.164$ min^{-1}) was remarkably higher than that of CS ($k_1 = 0.002$, $k_2 = 0.007$ min^{-1}). Similarly, the P adsorption capacity of CF500 ($q_{e1} = 1.96$, $q_{e2} = 1.99$ mg/g) was superior to that of CS ($q_{e1} = 0.150$, $q_{e2} = 0.234$ mg/g). The obtained results highlight the great potential of CF500 with regard to both P removal rate and P binding ability. Contrarily, these properties can be significant drawbacks of CS as a wetland substrate. Based on the correlation values (R^2), it can be concluded that both Pseudo first–order and Pseudo second–order models were suitable for describing the adsorption kinetic data of CS, whereas the latter was better than the former in describing the adsorption kinetic data of CF500.

Table 3

The isotherm study reveals the adoption capacities of filter materials. The isotherm parameters of CS and CF500 are presented in Table 3. It was discovered that the experimental isotherm data of CS was better fitted to the Freundlich isotherm model with higher R^2 value (0.969). In contrast, the quite similar R^2 values showed that both Langmuir and Freundlich models were suitable for describing isotherm data of CF500. The maximum adsorption capacity of CF500 (19.4 mg/g) was 9–fold greater than that of CS (2.12 mg/g). CF500 exhibited a greater P sorption capacity (19.4 mg/g) than some other filter materials, such as limestone (0.666 mg/g), bricks (0.451 mg/g), steel slag (2.863 mg/g) [10], and thermally-treated calcium-rich attapulgite (5.99 mg/g) [29]. Since CF500 was superior to CS and other filter materials in terms of P retention capacity, CF500 exhibited a high potential as a filter material to augment constructed wetlands' ability to treat P.

Thermodynamic study provides information about the nature of the adsorption process. Since CS demonstrated extremely poor P sorption ability, this study only explored thermodynamic parameters of CF500 (Table 4). The values of ΔG° at 30, 40 and 50 ^{o}C were -2954, -3215 and -3427 J/mol, respectively. The negative values of ΔG° indicate that the P sorption onto CF500 was spontaneous and feasible [25]. The positive ΔH° (+4224 J/mol) confirmed endothermic nature of the process. Since ΔH value did not belong to the typical range of ΔH for chemisorption (40–120 kJ/mol), the P sorption onto CF500 can be physical sorption [30]. The positive value of ΔS° (24 J/mol/K) reflected high affinity of CF500 for PO_4^{3-} anions, and more randomness at the solid–liquid interface during the sorption process [25].

Table 4

3.2.2. Physicochemical properties of CS and CF500

The physicochemical properties of CS and CF500 are presented in Table 5. It is clear that the hydraulic conductivity of CF500 (0.006 ± 0.0005 cm/s) was significantly lower than that of CS (4.06 ± 0.1 cm/s) ($p < 0.001$). Compared with other wetland substrates, it was nearly equivalent to that of the fine sand (0.001 to 0.01 cm/s) [31] but inferior to gravel (0.2 cm/s) [23], laterite of 1.4–5.6 mm (0.5 cm/s), limestone of 1.4–2.0 mm (0.6 cm/s), and coarse sand (0.01 to 1 cm/s) [31]. The low hydraulic conductivity of CF500 can pose a risk of water clogging to the wetland, where CF500 is solely employed as the substrate. In contrast, CS exhibited the better hydraulic conductivity than some common wetland substrates as mentioned above, indicating its excellent ability to prevent water clogging. This highlights the potential of combining CF500 and CS to satisfy key requirements of potential wetland substrates.

Table 5

Relating the chemical composition of CS and CF500, the investigated parameters included pH, organic matter, P_{total}, $P_{available}$, $Fe_{oxalate}$, and $Al_{oxalate}$.

The use of filter materials can affect pH of the aqueous solutions. As shown in Table 5, CF500 resulted in a slightly acidic medium (pH_{H2O} = 6.18 ± 0.12), whereas CS produced a slightly basic medium (pH_{H2O} = 7.32 ± 0.25). Thus, as a result of combining CS and CF500, the pH of the treated wastewater will be in the neutral range, which favors the growth of plants and microorganisms [32].

Organic matter is one of main factors influencing the P sorption capacity of a filter material. Organic materials including humic substances and some organic acids (e.g. malic, oxalic, and fulvic) can react with dissolved Fe & Al, leading to a reduction in the amounts of Fe & Al available for P retention [17]. Consequently, the P sorption capacity of a filter material decreases when the amount of organic matter increases. As summarized in Table 5, the percentages of organic matter in both CS and CF500 were very low (< 0.08%). This can be considered an advantage of these materials for P sorption. The smaller amount of organic matter in both CS and CF500 can be explained by the fact that due to the effect of high temperature during calcination or combustion, organic matters in CS and CF500 were degraded into CO_2 and H_2O, which vapored into the air.

Bio–available P is another indicator for P binding ability of a filter material. The higher bio–available P content in a filter material can lead to poorer P sorption capacity. This is because in the filter material, P can easily react with the available Fe/Al to form precipitation as the amorphous or poorly crystalline solids. High levels of phosphate and cations enable these reactions to occur. In the wetland medium, some major mineral precipitates are

Variscite $Al(PO_4).2H_2O$, Strengite $Fe(PO_4).2H_2O$, Vivianite $Fe_3(PO_4)_2.8H_2O$ and Wavellite $Al_3(OH)_3(PO_4)_2.5H_2O$ [8]. As a consequence, less Fe/Al are available for P retention. It is observed from Table 5 that, both CS and CF500 were very poor in bio–available P contents. This property may favor P sorption by these filter materials.

As mentioned above, organic matter and bio–available P contents in a filter material were found to be inversely proportion to its P retention capacity. In contrast, large amounts of oxalate extractable Fe & Al are reported to enable P sorption ability of a filter material. As shown in Table 5, the contents of $Fe_{oxalate}$ and $Al_{oxalate}$ in CS (0.273 ± 0.012 and < 0.004 mg/g) were much lower than those in CF500 (2.28 ± 0.11 and 2.12 ± 0.06 mg/g). These results are consistent with the isotherm data, indicating that the q_{max} value of CS (2.12 mg/g) was inferior to that of CF500 (19.4 mg/g). This indicates that the contents of $Fe_{oxalate}$ and $Al_{oxalate}$ in a filter material are good indicators for its P adsorption ability. This finding is useful for screening of filter materials to be used in constructed wetlands for P removal. Since the q_{max} value of CF500 was 9.14 times higher than that of CS, the presence of CF500 in the substrate mixture is expected to intensify the P removal efficiency of the hybrid substrate based HSSF-CW2,3,4 compared to that of single CS based HSSF-CW1. Hence, the P sorption capacity can be considered as the disadvantage of CS but the advantage of CF500.

In short, both CS and CF500 have their own merits and demerits. It is important to note that advantages of CS (e.g. good hydraulic conductivity, poor P sorption capacity, and slightly basic pH) are disadvantages of CF500 (e.g. low hydraulic conductivity, high P sorption capacity, and slightly acidic pH). Consequently, there is a high possibility that the combination of CS and CF500 can overcome the drawbacks of single filter materials.

3.3. Applicability of the hybrid mixed substrate in HSSF–CWs for P decontamination

3.3.1. Selection of the best mixing ratio

This study characterizes two different substrates and evaluates the ability to use their mixture as a hybrid substrate in HSSF–CWs for P–rich wastewater decontamination. The results showed that each investigated substrate had its own advantages and disadvantages. Of which, the latter may hinder their application as a single substrate. Specifically, CF500 was characterized by high P retention capacity (q_{max} = 19.4 mg/g) but low hydraulic conductivity (K = 0.006 ± 0.0005 cm/s). In contrast, although CS possessed a very low P sorption capacity (q_{max} = 2.12 mg/g), it demonstrated an excellent hydraulic conductivity (K = 4.06 ± 0.1 cm/s). Obviously, as a result of using these filter materials as single substrates, the HSSF–CWs have to face such problems as inefficient P removal (CS only) or poor water drainage (CF500 only). Thus, the combination of these two filter materials is expected to overcome the above problems.

Three mixing ratios of CF500 to CS (1:1, 1.25:1, and 1.5:1 by volume) were evaluated to select the best one. Since the P sorption ability of the mixture mainly relies on CF500, the higher the mixing ratio of CF500 to CS is, the better the P removal efficiency will be. However, the potential of water clogging can be exaggerated with the greater mixing ratio of CF500 to CS. Therefore, the selection of the best mixing ratio was necessary to ensure both maximum P removal and minimum water clogging. The results indicated that the mixing ratio of 1.5:1 can result in the highest P removal but also the lowest hydraulic conductivity (K = 0.015 ± 0.002 cm/s). Therefore, in order to minimize the risk of water clogging caused by small particle sizes of CF500, the mixing ratio of 1.25:1 with reasonably high P sorption capacity and notably efficient water conductivity (K = 0.031 ± 0.002 cm/s) was selected for the design of the lab–scale HSSF–CWs.

3.3.2. Phosphorus treatment performance of HSSF–CWs

To evaluate the treatment performance of HSSF–CWs, the concentration reduction percentage and mass removal are commonly used [8]. This study evaluates the P removal efficacy of HSSF–CWs based on three criteria: (i) average removal percentage (%), (ii) average removal rate ($g/m^2/d$), and (iii) wetland effluent concentration. A comparative study was conducted between HSSF–CW packed with single substrate (only CS) and HSSF–CWs filled with hybrid substrates (a mixture of CS and CF500). The average P removal efficiencies of HSSF–CWs are shown in Fig. 2a. It can be seen that all three HSSF–CWs using mixed combined substrates (CS and CF500) demonstrated the excellent removal of ortho P, being as high as 99.36 ± 0.46–99.55 ± 0.44% for removal efficiency and 0.416 ± 0.022–0.419 ± 0.018 $g/m^2/d$ for removal rate, respectively. In contrast, HSSF–CW packed with a single substrate (CS) had very poor P removal efficiency (21.91 ± 11.15%) and removal rate (0.111 ± 0.060 $g/m^2/d$). When compared to single substrate HSSF–CW, the hybrid substrate HSSF–CWs were 4–fold more efficient in P removal. This highlights the role of CF500 as an adsorptive material in the mixed combined substrates. This is consistent with another study conducted by [33], indicating that the P removal in HSSF-CWs was increased by 21% owing to the usage of adsorptive dolomite, $CaMg(CO_3)_2$ to replace sand as the substrate. As shown in Fig. 2a, the standard deviation values of the hybrid substrates HSSF–CWs were very low, which implied a stable treatment performance throughout the 4–month operation period. Contrarily, the high standard deviation value of the single substrate HSSF–CW indicated a high fluctuation of effluent P concentrations. The obtained results suggested that combining the two materials (CF500 and CS) revealed extremely good and stable P treatment efficiency.

Though the synthetic wastewater was lack of nitrate and carbon source, this might not affect the efficacy of hybrid substrate HSSF–CWs. That is because plants can exudate useful organic compounds (often citric and oxalic acids) for the microbial growth via their roots [34]. Additionally, autotrophic microbes can help with synthesis of organic matters via the following reaction:

$NH_4^+ + 1.815\ O_2 + 0.1304\ CO_2 = 0.0261\ C_5H_7O_2N + 0.973\ NO_3^- + 0.921\ H_20 + 1.973H^+$ (11)

When microbes die, they become a source of organic matters, which provide carbon sources for living microbe’s growth and activities [35].

Based on the q_{max} values of CS and CF500, the mass of these filter media, the volumetric flow rates, and the influent P concentration of the HSSF–CWs, it can be estimated that the lifespans for the single CS filter bed and hybrid CF500–CS filter bed are 3.0 and 23.7 years, respectively. However, in the reality, the P content captured per unit mass of a filter material can hardly reach its q_{max} value. This is due to the competing effects of plants, microorganisms, organic matter and suspended solids [36]. Additionally, the actual P concentration in the CWs influent is often substantially smaller than the P influent concentration range, which is used for determing the q_{max} value. Consequently, the use of the q_{max} value for estimating the lifespan of the filter bed can lead to an over estimation. To address this issue, it is suggested by [17] to utilize the real P adsorption capacity (q_{real}), accounting for 50% of the q_{max} value, alternatively. In this case, the expected lifespans for the single CS filter bed and hybrid CF500–CS filter bed are 1.5 and 11.8 years, respectively. The long life span of the hybrid CF500–CS filter bed explains why the P levels in the effluents of the CF500–CS hybrid substrate HSSF–CWs were stably low during 4–month operation period.

Figure 2

Fig. 2(a) indicates that the difference in the P removal efficiencies of HSSF–CW2 (planted with *A. ipomoea*), HSSF–CW3 (without any plant) and HSSF–CW4 (planted with *C. citratus*) were negligible, suggesting the minor role of plants in the P removal by HSSF-CWs. This can be explained by the fact that, in the initial stage of HSSF–CWs operation, when adsorptive CF500 material was not saturated, the adsorption sites on CF500 were abundant. As a result, CF500 played a pre–dominant role in the P removal by HSSF–CWs. A similar outcome was reported for P removal by the vegetated sequencing batch CS bed [17].

The results for P removal efficiency matched well with those on P concentrations of the effluents from HSSF–CWs. As can be seen in Fig. 2(b), the P outlet concentration from three hybrid substrate HSSF–CWs varied from 0.07 to 0.09 mg/L, which satisfied the discharge standard of 4 mg/L (QCVN40:2011/BTNMT [37], Class A). The extremely low P levels of the effluents from HSSF–CWs filled with hybrid substrates indicated their remarkable P removal. This can be attributed to a high P binding capacity of CF500. Conversely, the P concentration in the effluent of HSSF–CW packed with single substrate surpassed the permissible level of 6 mg/L (QCVN40:2011/BTNMT [37], Class B) from when the operation period commenced. This can be explained by poor P binding capacity of CS.

It should be noted that there was no water clogging in all HSFF–CWs during 4–month operation period. The mixture of CS and CF500 revealed great potential as a hybrid substrate because of its abilities to: firstly, efficiently sequester P from wastewater; and secondly, successfully prevent HSSF–CWs from water clogging. This suggests that the combination of CS and CF500 was essential to meet key requirements of potential wetland substrates.

3.3.3. Side effects of using substrates on effluent quality

Though hybrid substrates can significantly improve the P treatment performance of CWs, their wide application may be hindered due to possible side effects on the effluent quality. This study examines the quality of the effluents from HSSF–CWs filled with a mixture of CF500 and CS with regard to pH, EC and heavy metal concentrations.

The average pH values of the effluents from HSSF–CWs as well as the influent are depicted in Fig. 3. It can be observed that the pH average value of the effluents from all HSSF–CWs were near neutral or slightly alkaline zone. Though the pH values of the effluents (7.23 ± 0.21–7.48 ± 0.23) were found to be a little bit higher than that of the influent (6.76 ± 0.26), they are still in the permissible range (5.5–9.0) according to QCVN40:2011/BTNMT [37] (Class B). Thus, the effluent from HSSF–CWs packed with the hybrid substrate (CF500 and CS) can be safely discharged into the environment without any detrimental effects of pH. Similarly, it was recently reported that the mean pH value of the effluents from vertical flow constructed wetlands (VF–CWs), which was filled with layered combined bio–ceramic, zeolite, and anthracite, was in the neutral range of 7.07–7.15 [11].

Figure 3

Since CS is an industrial by–product and CF500 is known to be abundant in Fe & Al oxides, there is a concern that their uses as wetland substrates may not be environmentally safe owing to the probable release of heavy metals in aqueous solutions. To confirm this assumption, this study examined both EC and heavy metal concentrations in the effluents from HSSF–CW units. The EC value of water is the ability of water to pass the flow of an electrical current. This ability is directly dependent on the concentration of conductive ions present in the water. EC is directly proportional to salinity, hardness and total dissolved solids (TDS). EC measurement was considered as a convenient method for fast determination of the total concentration of metal ions [38]. In this study, EC was utilized to predict an increase in the levels of metal ions, which were possibly released into the solution from wetland substrates. It is evident from Fig. 3 that the difference in the EC values of the influent (1278 ± 63 µS/cm) and the effluents of HSSW–CW2 (1311 ± 95 µS/cm), HSSF–CW3 (1303 ± 96 µS/cm), HSSF–CW4 (1310 ± 98 µS/cm) was insignificant $(p > 0.05)$. On the contrary, the difference in the EC values of the influent (1278 ± 63 µS/cm) and the effluent of HSSW–CW1 (1456 ± 74 µS/cm) was significant $(p < 0.001)$. The EC results implied that the concentration of metal ions in the effluent of the single (CS) substrate HSSF–CW1 might be lower than those of the hybrid CF500–CS substrate HSSF–CW2, HSSF–CW3, and HSSF–CW4.

Table 6 represents concentrations of the most common heavy metals in the effluents from all HSSF–CWs. It was discovered that the levels of all metals in the effluents from all four HSSF–CWs were far below the discharge standards as recommended by QCVN40:2011/BTNMT for industrial wastewater [37]. This finding agrees well with the aforementioned results on EC values of the wetland effluents. Accordingly, the release of heavy metals from CS and CF500 into aqueous solutions during a 4–month operation period was negligible. As this study was performed in a short period, it is recommended to monitor the possible release of heavy metals during the long term use of the hybrid CF500–CS substrate HSSF–CWs to ensure the safety of their effluents.

Table 6

4. Conclusions

Calcination was found efficient in enhancing P sorption ability of NF. CF500 showed 60.4 ± 2.2% better P retention capacity than NF, which is attributed to differences in morphology, mineral composition, and physicochemical properties. While isotherm data for P sorption onto CF500 were fitted with both Langmuir and Freundlich models, the kinetic data was more satisfactorily described by Pseudo–second–order model. The mixture of CS and CF500 exploited advantages of individual substrates while mitigated their demerits, thereby satisfying crucial requirements for a potential wetland substrate. The best mixing ratio of CF500 to CS was 1.25:1 by volume. The CF500–CS composite substrate HSSF–CWs exhibited high P removal efficiencies (99.44% ± 0.1) and low P effluent concentrations (0.08 ± 0.01 mg/L), which represented clear differences with the CS single substrate HSSF–CW. The side effects resulted from using the hybrid substrate on the wetland effluents were minor. These findings enable utilization of CS and CF500 as the mixed hybrid media in CWs for P removal from wastewater.

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FIGURE CAPTIONS

Figure 1

XRD analysis results of a) NF and b) CF500.

Figure 2

a) The P removal efficiencies of single and hybrid substrate HSSF-CWs, and b) The P concentrations in the effluents of single and hybrid substrate HSSF-CWs over the time.

Figure 3

The pH and EC values of the HSSF-CWs packed with single and hybrid substrates.

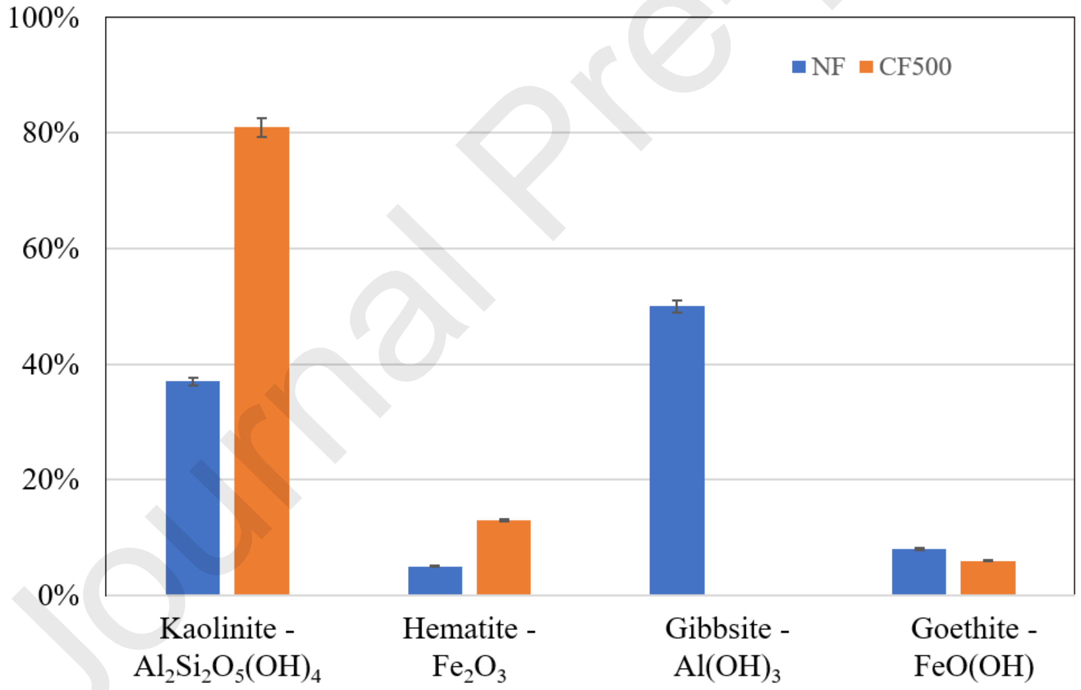
100%
80%
60%
40%
20%
0%
NF
CF500
Kaolinite - $Al_2Si_2O_5(OH)_4$
Hematite - Fe_2O_3
Gibbsite - $Al(OH)_3$
Goethite - FeO(OH)

Figure 1

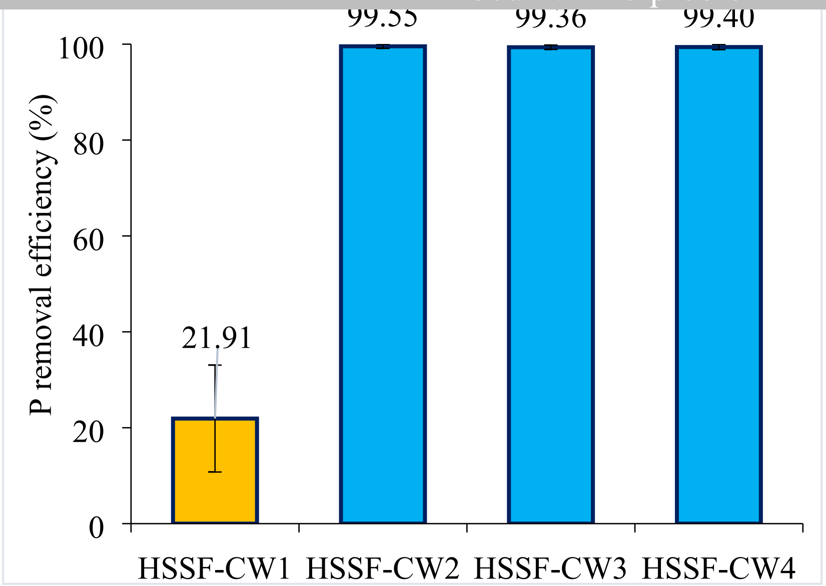

Figure 2a

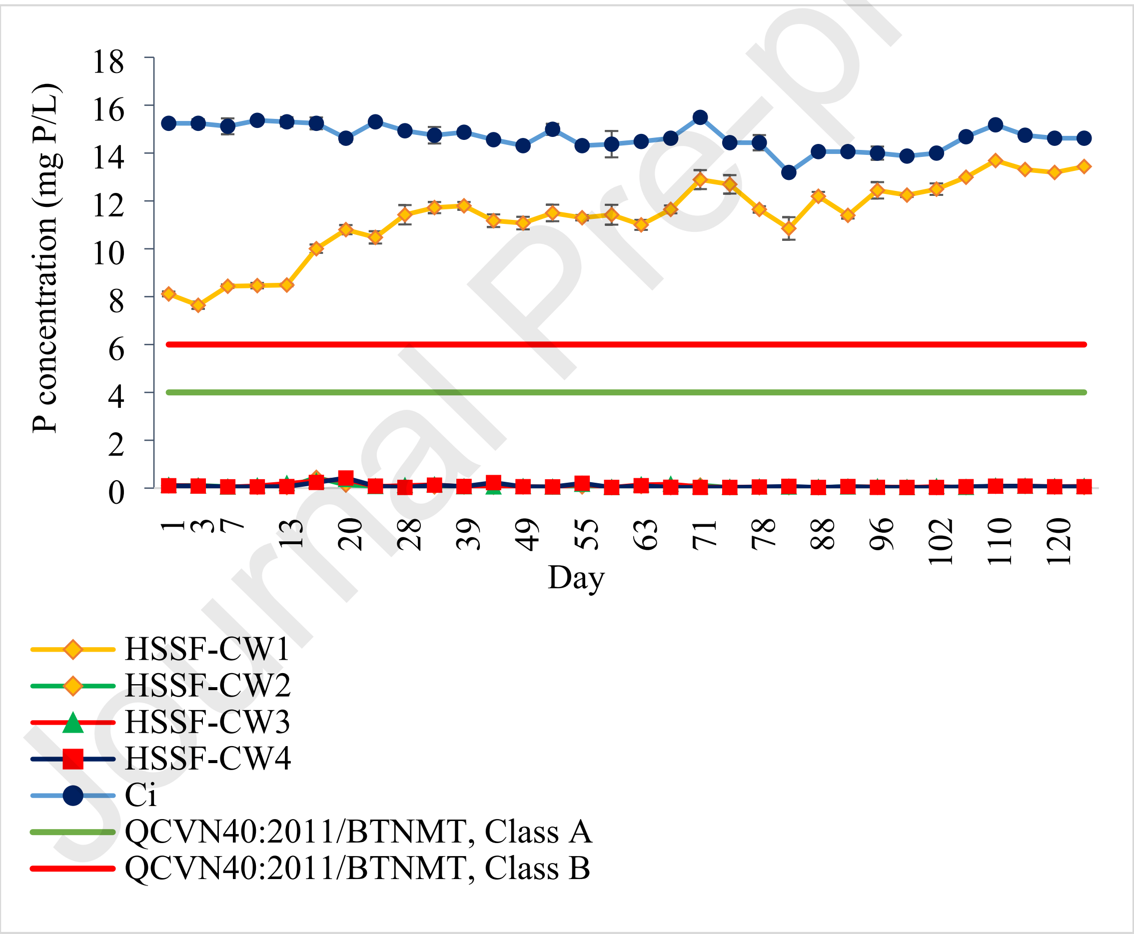

Figure 2b

Figure 2

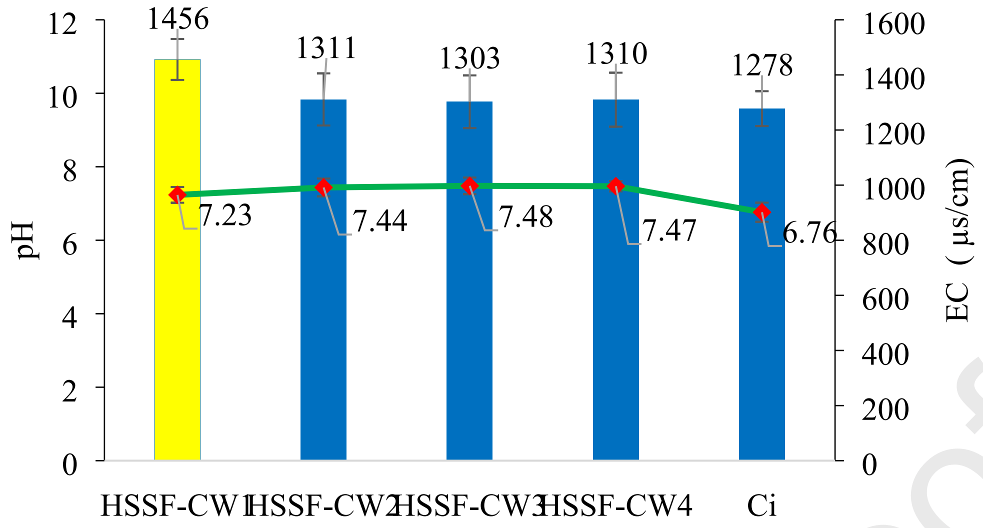

Figure 3

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TABLES

Table 1

Conditions for batch adsorption tests of CF300, CF500, CF700, and CS.

Experiment	Material	Process parameters
Selection of calcination temperature	CF300, CF500, CF700	Initial P concentration = 200 mg/L, adsorbent dose = 3 g/75 mL, temperature = 25 °C, shaking speed = 120 rpm, contact time = 24 h, pH = 3
Isotherm test	CF500, CS	Initial P concentration = 10-1000 mg/L, adsorbent dose = 1 g/75 mL, temperature = 25 °C, shaking speed = 120 rpm, contact time = 24 h, pH = 3

Kinetic test	CF500, CS	Initial P concentration = 50 mg/L, adsorbent dose = 2 g/75 mL, temperature = 25 °C, shaking speed = 120 rpm, contact time = different time intervals, pH = 3
Thermodynamic test	CF500	Initial P concentration = 10-1000 mg/L, adsorbent dose = 1 g/75 mL, temperature = 30, 40, 50 °C, shaking speed = 120 rpm, contact time = 24 h, pH = 3

Table 2

Chemical composition of NF and CF500 (wt.%).

Components	NF	CF500
SiO_2	28.0	29.7
TiO_2	4.15	4.40
T- Fe_2O_3	21.8	22.9
Al_2O_3	30.5	35.4
Na_2O	< 0.01	< 0.01
K_2O	0.03	0.03
CaO	0.02	0.02
MnO	0.09	0.10
P_2O_5	0.17	0.21
SO_3	0.15	0.18
CuO	0.015	0.016
ZnO	0.014	0.015
NiO	0.023	0.025
Cr_2O_3	0.061	0.068
Loss on ignition	14.8	6.81

Note: The relative standard deviation was ± 2% of the obtained results.

Table 3

Adsorption isotherm and kinetic parameters of CS and CF500.

Adsorption isotherm parameters of CS and CF500						
Model	Langmuir			Freundlich		
Parameter	q_m (mg/g)	K_L (L/mg)	R^2	n	K_f (mg/g)(L/mg)$^{1/n}$	R^2
CS	2.12	0.001	0.956	1.15	0.005	0.969
CF500	19.4	0.008	0.982	2.35	1.10	0.980
Adsorption kinetic parameters of CS and CF500						
Model	Pseudo-first-order			Pseudo-second-order		
Parameter	q_{e1} (mg/g)	k_1 (1/min)	R_1^2	q_{e2} (mg/g)	k_2 (g/mg/min)	R_2^2
CS	0.150	0.002	0.983	0.234	0.007	0.984
CF500	1.96	0.247	0.932	1.99	0.164	0.949

Table 4

Thermodynamic parameters for P adsorption on CF500.

Temperature (°C)	q_m (mg/g)	K_d	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/mol/K)
30	19.6	3.23	-2954	4224	24
40	21.3	3.44	-3215		
50	23.5	3.58	-3427		

Table 5

Physicochemical properties of CS and CF500.

Parameter	Unit	CS (1.4–5.6 mm)	CF500 (< 2.8 mm)
Hydraulic conductivity	cm/s	4.06 ± 0.1	0.006 ± 0.0005
Porosity	%	57.0 ± 0.3	51.3 ± 0.6
Particle density	g/cm^3	1.91 ± 0.02	2.15 ± 0.04
pH_{H2O}	-	7.32 ± 0.25	6.18 ± 0.12
Organic matter	%	< 0.08	< 0.08
Total P	% P_2O_5	0.015 ± 0.001	0.085 ± 0.005
Bio-available P	mg P_2O_5/100 g material	1.32 ± 0.04	0.850 ± 0.02
$Fe_{oxalate}$	mg/g	0.273 ± 0.012	2.28 ± 0.11
$Al_{oxalate}$	mg/g	< 0.004	2.12 ± 0.06

Table 6

Heavy metal concentration (mg/L) in the influent and effluents from HSSF-CWs.

Heavy metal	Influent concentration (mg/L)	Effluent concentration (mg/L)				QCVN 40:2011/BTNMT (Class B)
		HSSF-CW1	HSSF-CW2	HSSF-CW3	HSSF-CW4	
Al	0.040	0.033	0.061	0.020	0.035	-
As	0.030	0.032	0.040	0.040	0.002	0.1
Cd	0.003	< 0.002	< 0.002	< 0.002	< 0.002	0.1
Cu	0.020	< 0.002	< 0.002	< 0.002	< 0.002	2
Fe	< 0.002	0.210	0.016	0.008	0.078	5
Hg	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	0.01
Pb	< 0.002	0.020	0.004	0.038	< 0.002	0.5
Zn	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	3

Note: The relative standard deviation was ± 2% of the obtained results.

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GRAPHICAL ABSTRACT