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Enhanced Removal of Phosphorus from Aqueous Solutions by Cation-Modified Hydrochar

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Abstract

In this study, cassava stem-derived hydrochar was modified with sodium hydroxide (NaOH) treatment, followed by loading of minerals, was used to prepare cation-modified hydrochars with enhanced phosphate removal ability. Cassava stems were converted to hydrochar by hydrothermal carbonization at 240 °C for 60 min, then it was soaked in 2 M NaOH for 3 h. The NaOH-treated hydrochars were then loaded with iron (Fe), magnesium (Mg) and calcium (Ca). The cassava stems and the derived hydrochars were analyzed for carbon, hydrogen, nitrogen and oxygen content, surface morphology and elemental compositions. Methylene Blue Numbers (MBN) measured surface area and porosity, and pH at the point of zero charge (pHpzc) was determined. Modification with Fe, Mg and Ca improved phosphate removal efficiency of the resulting hydrochars. Treatment of synthetic wastewater containing 50 mg P/L at pH 7 with the dosage of 2 g/L of the cation-modified hydrochars for 360 min showed that phosphate removal efficiency of these modified hydrochars were - Fe-modified 81 %, Mg-modified 66 % and Ca-modified 56 %. When the adsorbent dosage increased to 20 g/L, more than 98 % of phosphate was removed by the hydrochars modified with Fe, Ca and Mg. In the same conditions, phosphate removal efficiency was for the NaOH-treated hydrochars - 89 %, hydrochar derived from cassava steam - 69 % and the starting material - 59 %. The phosphate removal ability of these cation-modified hydrochars increased even when initial phosphorus concentration was increased to 100 mg P/L. This work demonstrated that an abundant agricultural residue, cassava stems, can be converted into effective phosphate adsorbents.

Keywords: Hydrochar, Hydrothermal carbonization, Chemical modification, Nutrient removal, Phosphorus

Introduction

Phosphorus is vital for food production, since it is one of 3 essential nutrients (nitrogen, potassium and phosphorus) needed for plant growth. With proper availability of soil nutrients, plants will grow and thrive, however, nitrogen (N), phosphorus (P) and potassium (K) are often insufficient in soil. As a result, these chemicals are added to soil as fertilizer to enrich the soil nutrients, thus promoting plant growth and productivity. Most of the phosphorus in fertilizer comes from phosphate rock, a finite resource, formed in the earth's crust over millions of years [1,2]. While the demand for phosphorus in the production of food crops increases every year to keep up with the increase in food demand from population growth, there has been a concern over the depletion of phosphate resources [3]. In addition, the reserves are mostly located in northern Africa, especially Morocco and Western Sahara [1,2]. Finding alternate phosphorus sources is an interesting topic since it offers a sustainable solution to the phosphorus shortage. Among several sources, phosphorus recovery from wastewater receives increasing attention. Wastewater and effluents, from agricultural, municipal and industrial sources, are important sources of phosphorus loading on aquatic environments. Low phosphorus concentrations are necessary for the biological health of aquatic ecosystems; however, excessive phosphorus inputs to water bodies cause eutrophication, leading to a serious deterioration of water quality. Thus, phosphorus removal and recovery from phosphate-rich wastewater offers a viable solution to address the scarcity of phosphorus for agriculture production and mitigate eutrophication problems in the receiving environment.

Adsorption is an effective water treatment option due to its convenience, ease of operation, simplicity of design and economics [4]. However, the application of adsorption to wastewater treatment plants is often limited by the necessity to regenerate sorbents and discharge the regeneration solution. With a greater emphasis on removing phosphorus down to very low concentrations and potentially recovering it from the effluent, adsorption has become one of the most attractive technologies used for phosphorus reclamation from wastewater [4-6]. Several adsorbents including hydrochar, a stable carbon-rich solid product synthesized by hydrothermal carbonization (HTC), have therefore been considered to remove phosphate from water. Hydrochars have become increasingly attractive in several sectors as they can be derived from a wide range of feedstocks, including agricultural biomass wastes. In addition, preparing hydrochars by HTC needs milder conditions than for slow pyrolysis, which typically requires elevated temperatures of 300 - 700 °C in the absence of oxygen [7], whereas HTC requires 180 to 260 °C with biomass immersed in water and heated in a confined system under pressure (2 - 6 MPa) [8], thus hydrochars have lower costs than biochar or activated carbon based adsorbents [9]. Another attractive feature of the HTC process is that it is carried out in the presence of water, thus, eliminating pre-drying requirements of wet biomass, which is energy-intensive and a financial burden in pre-processing, particularly when using conventional thermal pre-treatments such as slow-pyrolysis [8]. Since there is growing interest in using hydrochars as adsorbents for phosphorus removal and recovery from wastewater, however, the poor surface area and porosity of the pristine hydrochar [8], and a high number of oxygen-containing groups on the surface [7,10,11] limit its ability to be an effective adsorbent to capture phosphates from the water. Thus, modification techniques to improve the surface properties of hydrochar is required, allowing the enhancement of phosphate removal efficiency of hydrochar.

Hydrochar is rich in oxygen-containing functional groups (OFGs), resulting in higher adsorption capacity for the contaminants, especially positively charged contaminants [12]. On the other hand, the adsorption capacity of hydrochar for anions (i.e., phosphate, nitrate and arsenate) is very limited due to a large amount of OFGs, making the hydrochar surface more negatively charged, subsequently repelling negatively charged compounds [12]. To be used as a phosphate adsorbent, the surface of hydrochars must be modified to improve their ability to adsorb anions such as phosphates. Modification of hydrochars with La, Al, Mg, Ca and Fe or Layer Double Hydroxides (LDHs) has been demonstrated to effectively improve its ability to adsorb phosphates [6,9,13-15]. During the HTC process, modification needs 1 single step [6,13] or, at most 2, after carbonization [14,15]. These studies showed that phosphate adsorption significantly improved in chemically modified hydrochars compared to unmodified ones. In addition, treatment of hydrochars with NaOH promoted the formation of mesopore volume in the modified chars [16] and enhanced the oxygen-containing functional groups on their surface [17] which offered more adsorption sites for chemical elements, such as Fe, Ca and Mg, that are coated on the hydrochar to increase phosphate removal. Islam *et al.* [7] modified coconut shell-derived hydrochar by NaOH treatment using hydrochar: NaOH ratio of 1:3 for 4 h to obtain mesoporous carbon having a surface area of 876 m^2/g and an average pore diameter of 2.9 nm. Although NaOH treatment of hydrochars and modification by loading with different cations has been investigated, physicochemical properties and phosphate removal capacity of hydrochar produced from the sequential steps of HTC, alkali treatment and chemical modification have not been explored. In this study, cassava stems, residues left in the field after cassava root collection, were used as feedstock to produce hydrochar by HTC, followed by NaOH treatment and cation modification.

Cassava is an agro-industrial crop in Thailand, with a well-developed industry and market [18]. The primary parts of a cassava plant include the leaves, stems, rhizomes and roots. The most used part of the plant is the root, so the rest of the plant usually becomes waste. The biomass of the stems can be as much as 50 % of the root mass [18]. From the total amounts of all cassava stem residues, 20 % are collected post-harvest for the planting stock, and 29 % are used as fertilizer, and use of the remaining stems has so far been overlooked [18]. Thus, more research on use of the stems is needed. To date preparation of hydrochar from cassava stems, and its use in phosphate removal has been little reported. The overall purpose of this study is to convert cassava stems, an abundant agricultural solid waste into a value-added product with environmental application in water and wastewater, specifically (1) to produce pristine hydrochar from cassava stems by hydrothermal carbonization, treated with NaOH, followed by modification with 3 elements - Fe, Mg and Ca; (2) to compare physicochemical properties and phosphate adsorption characteristics of the prepared hydrochars, and (3) to measure phosphate removal and recovery of these modified hydrochars.

Materials and methods

Preparation of cassava stem

Stems of cassava plants, removed as waste from plantations, were peeled and cut into small pieces. The stems were rinsed and cleaned with tap water several times, following drying in the sun and milling.

Following milling, the material was sieved through a 70-mesh sieve prior to use and labeled "Cassava Stem Powder (CSP)".

Hydrothermal carbonization and NaOH pretreatment procedures

Hydrothermal carbonization (HTC) of the 70-mesh cassava stem powder used a 1 L Parr stirred pressure reactor, equipped with a heating system and a temperature controller (Parr Instrument Co., USA), following Thawornchaisit *et al.* [15]. During HTC, 35 g powder was mixed with deionized (DI) water at a ratio of 1:10 cassava stem powder:water (w/v). Before the reaction, residual air was removed from the sealed vessel by repeatedly purging it with nitrogen. The reactor and contents were then heated while stirring. The HTC temperature was set at 240 °C, with a holding time of 60 min. At the end of the holding time, the reactor was cooled to 45 °C. The hydrochar and hydrolysate were separated by vacuum filtration. The obtained hydrochars, labeled "original HC", were washed with deionized water, followed by oven drying at 105 °C for 24 h.

The original HC samples were chemically pretreated to improve their surface area following Tang *et al.* [19]. Briefly, 20 g original HC was soaked in 2 M NaOH solution at a solid:liquid ratio of 1:20 for 3 h. The resulting hydrochar, labeled "NaOH-HC", was washed with distilled water until the pH of the filtrate was neutral. The samples were dried in an oven at 105 °C for 24 h, and subsequently ground into a fine powder with a mortar. The resulting hydrochar samples were used as host materials for the preparation of cation-modified hydrochars.

Synthesis of modified hydrochar

Modified hydrochar was synthesized by impregnation of Ca, Mg and Fe on the NaOH-HC in an alkaline condition, following Yang *et al.* [20] with some modifications. To prepare modified hydrochar containing similar adsorbed amounts of Fe, Ca, or Mg, the aqueous solutions of 0.5 M $FeCl_3$, 1 M $CaCl_2$, and 1 M $MgCl_2$ were prepared. Next, 20 g NaOH-HC sample was immersed in the solution of the target ion at a solid-to-liquid ratio of 1:30. The mixture was stirred at 150 rpm for 10 min, followed by dropwise addition of 1 M NaOH until it reached pH 11. The suspension was continuously stirred for 2 h and aged without stirring for 24 h. The slurry was vacuum filtered. The separated solids were washed with deionized water until the pH of the washing solution equaled the pH of the water (pH 6.0 - 6.5) and oven-dried (105 °C, 24 h). The final products were labeled Ca-HC, Mg-HC and Fe-HC.

Characterization of materials

The C, H, N and O contents of CSP and original HC were analyzed in duplicate in an elemental analyzer (Flash Smart, Thermo Scientific, USA). For each element, relative percent difference (RPD) was calculated to compare the difference between 2 results obtained from duplicate analysis. The surface morphology of the cassava stem powder and the derived hydrochars were examined with a scanning electron microscope (SEM, QUANTA FEG-250, FEI, USA). Surface elemental analysis was determined simultaneously at the same spot using an energy-dispersive X-ray analyzer (EDS/EDX). Methylene Blue Number (MBN), defined as the maximum amount of dye adsorbed on 1.0 g of adsorbent, was used as an indicator of the surface area and porosity of the material. The MBN values were obtained from the adsorption studies of CSP and the derived hydrochars following Nunes and Guerreiro [21]. For each material, 3 independent adsorption tests (n = 3) were run. Briefly, about 10 mg tested material was placed in contact with 10 mL methylene blue solution at concentrations (10, 20, 30, 40 and 50 mg/L) for 24 h. The remaining concentration of methylene blue (Ce) was analyzed using a UV/Vis spectrophotometer at 667 nm. The amount of methylene blue adsorbed for each solution (q_e) was calculated, and the data was used to make a q_e plot as a function of C_e using the Langmuir model. MBN or the maximum dye adsorption capacity (q_{max}) for each material was found from a least squares regression. The pH at the point of 0 charge (pH_{pzc}) of CSP, original-HC, and the modified hydrochars was determined using the pH drift method [22]. A single measurement was determined for each sample. pH_{pzc} was determined by adjusting the pH of 50 mL 0.01 M NaCl solutions, from pH 3 to 11 at unit steps and noting the initial pH (pH_i). Then, 0.15 g of the tested material was added to an Erlenmeyer flask (shaken at 120 rpm, 24 h). The final pH (pH_f) of the solutions separated by centrifugation was measured. The pH_{pzc} of a sample was the point where the difference between the final pH value and the initial pH value (pH_f - pHi) was 0.

Phosphates removal study

Batch adsorption experiments determined the phosphate removal capacity of the cassava stem powder and the derived hydrochars. Triplicate experiments on each material measured the effect of adsorption parameters: Contact time, 30 - 360 min; adsorbent amounts, 0.1 - 1.0 g, and initial phosphate concentrations, 5 - 100 mg P/L. Phosphate removal capacity was determined by mixing a known amount of each material with 50 mL phosphate solutions (pH 7, 50 mg P/L). The mixtures were shaken in a mechanical shaker at a constant speed of 150 rpm. After a defined contact times (30 - 360 min), the mixtures were immediately filtered through a 0.45 μm filter, and the concentration of phosphate in the filtrates was measured based on the 4500-P E: Ascorbic Acid Method [23], based on the specific reaction of ammonium molybdate and antimony potassium tartrate with orthophosphates in an acid solution, forming an antimony-phospho-molybdate complex. The complex was reduced to an intensely blue-colored complex by ascorbic acid whose color was proportional to the phosphorus concentration. Phosphate removals were determined by decrease of the phosphate amount in the solution.

Results and discussion

Characterization of CSP and the prepared hydrochars

Elemental composition by CHNO elemental analysis

Elemental compositions from CHNO analysis of raw material (cassava stem powder, CSP) and the derived hydrochars following hydrothermal carbonization are shown in **Table 1**. The carbon content of the hydrochar was significantly higher than the raw material, while the H content slightly decreased from 6.1 % (raw material) to 5.5 %. In addition, the oxygen content of the hydrochar was significantly lower than those of the raw material with a difference of –17 %. Reduction in the H and O content was observed for different biomasses under HTC treatments and was mainly attributed to dehydration and decarboxylation [24-26]. Thus, hydrothermal treatment was able to convert organic carbon in biomass materials to a carbon-rich solid product namely as hydrochar.

Table 1 Carbon, hydrogen, nitrogen and oxygen (CHNO) contents of cassava stem powder and the derived hydrochars (n = 2).

Samples	**Element (RPD$^{1/}$, %)**			
	C	**H**	**O**	**N**
CSP	43.1 (0.4)	6.1 (2.0)	46 5 (0.8)	0.88 (0.00)
Original HC	61.1 (0.1)	5.5 (1.8)	29.6 (0.2)	0.80 (0.05)

$^{1/}$Relative percent difference.

Surface morphology and elemental composition of the prepared materials by SEM-EDS

SEM images of cassava stem powder (CSP) and hydrochars are in **Figure 1**. The surface morphology of the biomass changed evidently following hydrothermal carbonization and chemical modification of the hydrochar. **Figure 1**(**a**) shows that cassava stem powder had a comparatively smooth surface, whereas the derived hydrochar surface was rougher with some cracks and crevices (Original-HC, **Figure 1**(**b**)). After treatment with NaOH, the NaOH-HC surface became rougher compared with the original HC as seen in **Figure 1**(**c**). Rough surfaces on NaOH-HC were observed because of the ability of NaOH to react with the ester bonds linking the lignin to the hemicellulose, leading to surface hydrolysis and degradation [27]. This characteristic should facilitate adsorption of chemicals in the water. After modification with cations, the hydrochar surface, especially Fe-HC (**Figure 1**(**d**)), became flattened. Surface elemental analysis was run with the SEM at the same surface locations using EDS to obtain semi-quantitative data on the elemental composition of the prepared materials. EDS analysis of the original HC (**Figure 1**(**b**)) revealed larger proportions of carbon with lower proportions of oxygen than those present in the CSP. These results matched the data from CHNO elemental analysis (**Table 1**) confirming that HTC converted cassava stem to a hydrochar which was rich in carbon. EDS spectra of the NaOH-HC (**Figure 1**(**c**)) revealed the presence of Na on the surface of the hydrochar confirming the reaction of NaOH with carbon in the hydrochar during the NaOH treatment. Zhou *et al.* [28] noted that interactions between NaOH and carbon during cold alkali treatment promoted the formation of micropores and mesopores in the NaOH-activated hydrochar, which subsequently led to an increase in surface area as well as adsorption capacity. For hydrochars modified with cations, the higher concentrations of Fe, Ca and Mg, shown in the EDS spectra (**Figures 1**(**d**) - **1**(**f**)), showed that these cations were successfully loaded on the NaOH-HC surface.

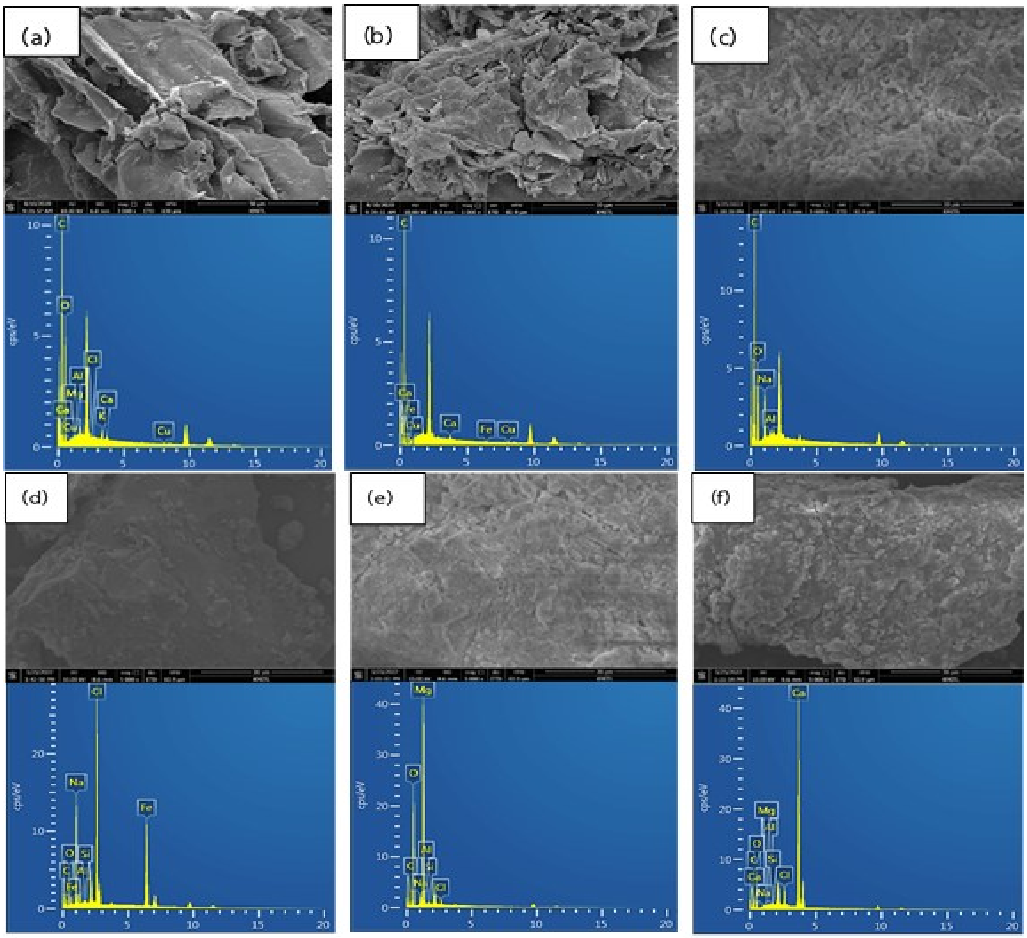

Figure 1 SEM images and the corresponding X-ray energy dispersive spectra (EDS) of the red selected region of (a) CSP, (b) original HC, (c) NaOH-HC, (d) Fe-HC, (e) Ca-HC and (f) Mg-HC.

Methylene blue number

The molecular size of methylene blue suggests that it is mainly adsorbed in mesopores, with a small amount present in larger micropores [21,29]. The adsorptions derived from MBN numbers are reported in **Table 2**. Obviously, the MBN of original HC was higher than that of CSP, indicating that HTC improved the aromaticity and porosity of HC. This observation was consistent with previous HTC research using lignocellulosic materials [15,30]. Furthermore, MBN of NaOH-HC was almost 4 times higher than the original HC, indicating the effectiveness of NaOH modification to improve the surface characteristics, with a further increase in surface area and porosity noted in the SEM-EDS analysis. After modification with Fe, Ca or Mg, the MBN of the cation-modified hydrochars generally decreased compared with the NaOH-HC. The MBN decrease was attributed to adsorption of Fe, Ca and Mg to the surface, enhancing its phosphate adsorption capacity.

Table 2 MBN and $\mathrm{pH_{pzc}}$ of cassava stem powder and prepared hydrochars.

Samples	MBN (mg/g)[1/]	$\mathrm{pH_{pzc}}$[2/]
CSP	24.6 ± 9.2	6.0
Original HC	45.0 ± 12.9	4.6
NaOH-HC	168 ± 10	9.0
Fe-HC	98.4 ± 7.2	8.3
Ca-HC	79.4 ± 7.9	9.0
Mg-HC	87.4 ± 5.5	8.3

[1/] Means from triplicates ± standard deviation.

[2/] Single measurement.

pH_{pzc}

The pH of point zero charges (pH_{pzc}) is the pH at which an adsorbent's surface charge equals 0 under specified temperature, pressure and aqueous solution components. It is one of the important properties of adsorbents that influences the proportion of adsorption [31]. Basically, the net surface charge on the solid surface for the adsorbent becomes positive when the solution pH is less than pH_{pzc} because of protonation of acidic groups. Therefore, coulombic attraction favors adsorption of anions like phosphates in water [31]. On the contrary, the surface charge becomes negative when $pH_{solution}$ exceeds pH_{pzc} due to the ionization or dissociation of acidic oxygen surface groups (such as carboxyl and phenolic), resulting in unfavorable conditions for adsorbing anions in water due to coulombic repulsion [31]. The pH_{pzc} of cassava stem powder (CSP) and the original hydrochar was below 7, while all chemically modified hydrochars had a pH_{pzc} above 8 (**Table 2**). This information would help to decide what solution pH will favor a particular adsorbent to remove phosphates from water.

Phosphate removal efficiency

Effect of contact time and modifying agents

The relationship between contact time and the phosphate removal capacity is shown in **Figure 2**. The removal ability of CSP gradually increased from 21 to 38 % as the contact time increased from 30 min to 180 min, thereafter phosphate removal remained unchanged for up to 360 min, indicating that the phosphate adsorption equilibrium had been reached. Similar trends were observed for the hydrochar derived from the cassava stem without any modification (original-HC), the iron-modified hydrochar (Fe-HC), and the calcium-modified hydrochar (Ca-HC). The increase in phosphate removal ability at the beginning of experiments was due to the availability of active sites on the adsorbents, thus phosphates quickly reacted, resulting in an increase in phosphate removal. As more and more of the surface area became saturated with phosphates, the phosphate removal rate slowed. The figure showed that only a small amount of phosphate was removed for contact times longer than 180 min. The NaOH-treated hydrochar (NaOH-HC) and magnesium-modified hydrochar exhibited a steady phosphate removal efficiency throughout the experiment duration up to 360 min, suggesting that phosphate adsorption kinetics of these hydrochars occurred at much faster rates than the others, thus no increasing trend was detected on the graph.

Figure 2 clearly shows that hydrothermal carbonization, followed by chemical modification, converted cassava stem powder (CSP) into an effective phosphate adsorbent. CSP alone removed the smallest amounts of phosphates with 39 % phosphate removal after 360 min, followed the hydrochar without any modification (original-HC, 43 %) indicating that hydrothermal carbonization helped improve phosphorus removal. NaOH-treated hydrochar was more effective than that of the original HC: This was attributed to the change in surface morphology and a further rise in surface area and pore volume after NaOH treatment, as seen in both SEM and MBN analyses. Hence, alkaline treatment is a promising activation method for improving phosphate removal. Loading NaOH-HC with Fe, Ca or Mg further improved phosphate removal efficiency. Of the 3 metals tested, Fe^{3+} (Fe-HC) removed phosphates more effectively than added Ca^{2+} or Mg^{2+} (**Figure 2**). This was expected, Fe^{3+} as a hard acid, thus, can react and form stronger bonds with phosphates (PO_4^{3-}) which are hard bases. Similar observations were reported by Thawornchaisit *et al.* [15].

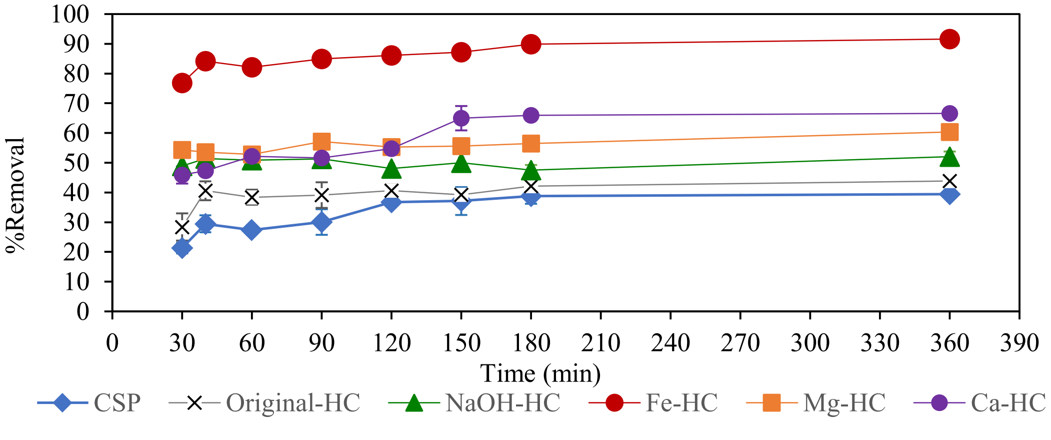

Figure 2 Phosphate removal efficiency of cassava stem, its derived hydrochar and cation-modified hydrochars for various times (adsorbent dosage: 2 g/L; initial P concentration: 50 mg P/L, pH 7).

Effect of adsorbent dosage

The effect of adsorbent dosage on the phosphate removal efficiency and the phosphate adsorption capacity (q_e) was investigated by varying concentrations of the tested materials from 2 to 20 g per liter of synthetic wastewater containing 50 mg P/L at pH 7. The reaction time was 360 min to ensure that adsorption equilibrium was reached in all runs. **Figure 3** shows that the phosphate removal efficiency increased with an increase in adsorbent dosage for all tested materials. At a dosage of 20 g/L, more than 98 % phosphate removal was achieved by the hydrochars modified with Fe, Ca and Mg. Whereas, at the same dosage (20 g/L), removal fractions were 89 % for NaOH-HC, 69 % for original-HC and 59 % for the original CSP. The increased removal with increased adsorbent dosage was attributed to the total number of accessible adsorption sites and surface area provided. At lower doses, limited active sites were available leading to a lower phosphate uptake capacity.

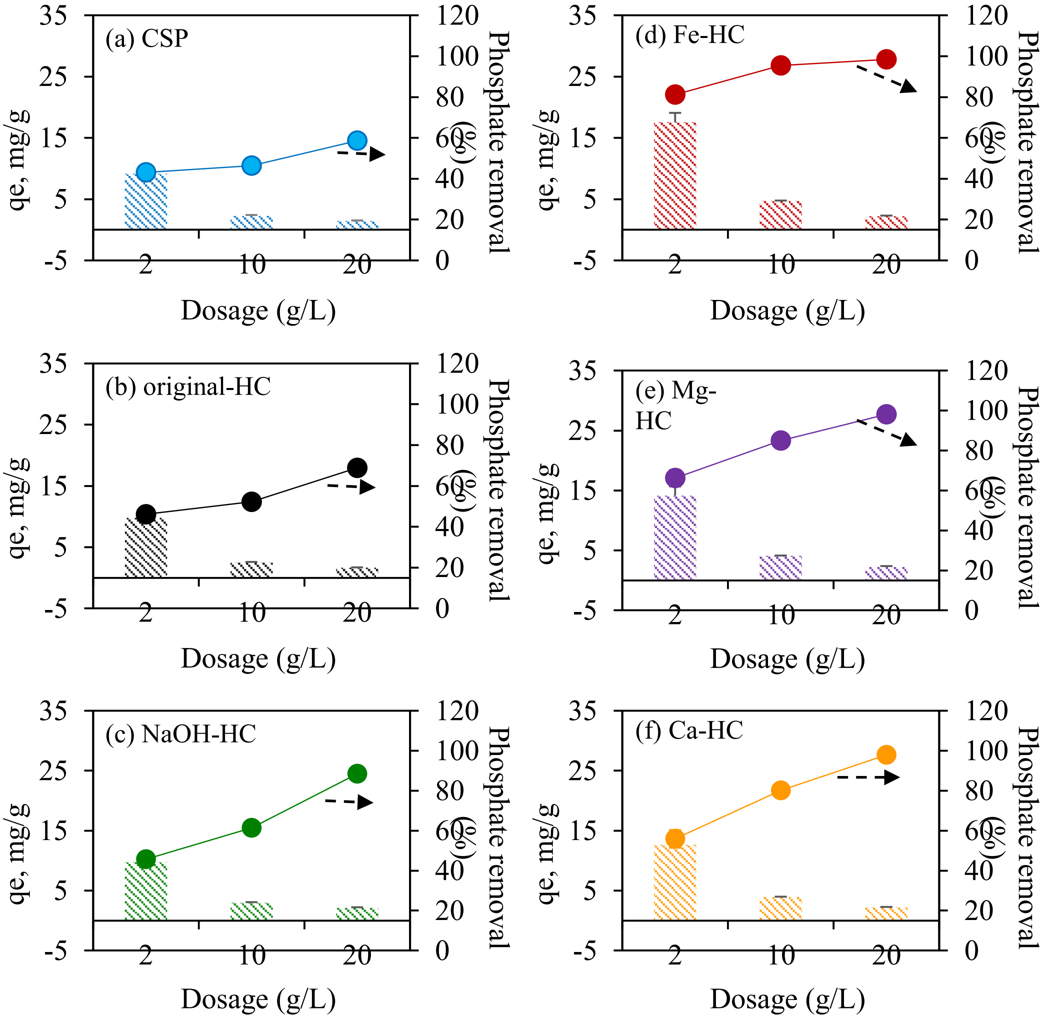

Figure 3 Effect of adsorbent dosage to phosphate adsorbed amount, q_e (bars with standard deviations) and phosphate removal (%) (circles) of cassava stem, its derived hydrochar, and cation-modified hydrochars. (Initial P concentration: 50 mg P/L, pH 7, contact time 360 min).

On the other hand, the amount of phosphate adsorbed per gram of the adsorbent (q_e), calculated by Eq. (1), decreased with adsorbent dosage. The decrease in q_e with the increase of adsorbent dosage, ***w***, was expected - see Eq. (1).

$$q_e = \frac{(C_0 - C_e)\times V}{w} \tag{1}$$

where q_e is the amount of phosphate adsorbed on a solid material (mg/g), C_0 and C_e are the initial and the equilibrium phosphorus concentrations, mg/L, respectively, V is the volume of solution (L) and w is the amount of adsorbent used (g). A similar relationship was also reported by He *et al.* [6] where increasing amounts of a MgAl-LDHs modified hydrochar was used as phosphate adsorbent. As the number of particles suspended increased with adsorbent dosage, particles aggregated, leading to the total effective adsorptive capacity of the adsorbent not being fully used, compared to those at a lower dosage [32], so phosphate adsorption decreased.

Effect of initial phosphate concentration

As shown in **Figure 4**, the extent of phosphate adsorbed per unit mass of adsorbent at equilibrium, defined as adsorption capacity (q_e), increased as the initial concentration of phosphates in aqueous solution (C_0) increased. Rising in phosphate adsorption capacity as an increase in initial concentration was attributted to higher driving forces provided by the higher initial concentrations, resulting in better filling of reactive adsorption sites [33,34]. In addition, the phosphate adsorption ability of cation-modified hydrochars was been significantly improved compared to CSP, original HC and NaOH-HC (**Figure 4**). It was discovered that the removal of phosphate increased with an increase in initial phosphate concentration in Fe-HC, Mg-HC and Ca-HC, implying that modification with cations was an efficient method to alter the hydrochar surface properties, thereby improving their removal performance.

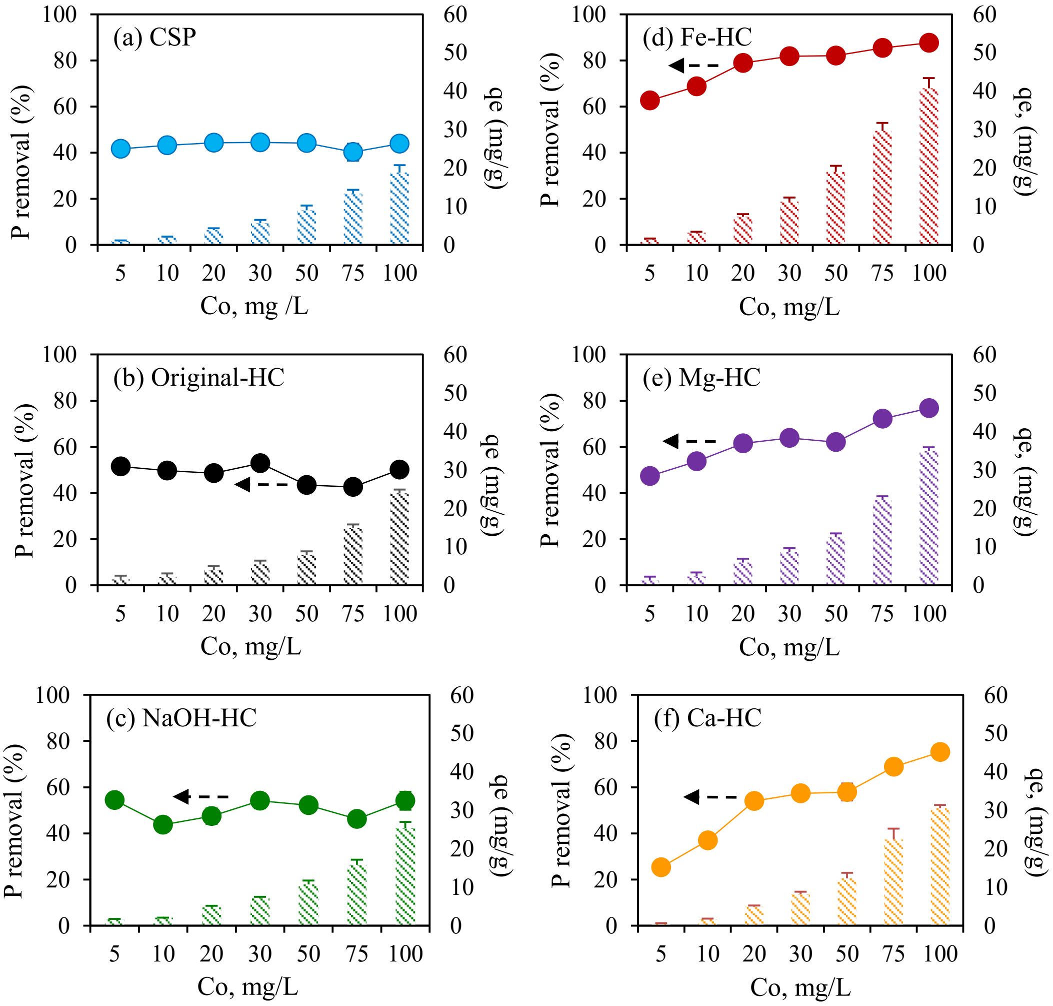

Figure 4 Phosphate removal ability (%) (circles) and absorption capacitis, q_e (bars with standard deviations) for cassava stems alone, its derived hydrochar, and the cation-modified hydrochars at different initial phosphate concentrations (adsorbent dosage: 2 g/L, pH 7, contact time 360 min).

Conclusions

In the present study, hydrothermal carbonization (HTC) followed by alkali treatment using sodium hydroxide (NaOH) and loading with elements including iron (Fe), calcium (Ca) and magnesium (Mg) were applied to convert cassava stems into modified hydrochars that can be used as effective adsorbents for phosphate removal from aqueous solution. Hydrochar produced from hydrothermal carbonization at 240 °C for 60 min using a 1 L Parr reactor had a carbon content of 61 %, while 43 % of carbon was in cassava stems. After treatment with NaOH, methylene blue number (MBN) increased from 24.6 mg/g in the starting materials to 168 mg/g in the NaOH-treated hydrochar. Results from scanning electron microscopy and energy-dispersive X-ray analysis (SEM-EDS) showed weight percentages of 18 % Fe, 29 % Ca and 28 % Mg in the Fe-, Ca- and Mg-modified hydrochars, respectively, while a small amount of these elements were in the cassava-derived hydrochar and the raw materials. The observation confirmed the success of loading the NaOH-treated hydrochars with Fe, Ca and Mg. Batch adsorption tests showed that cassava stem removed the smallest amounts of phosphates with 40 % when using 2 g per liter of synthetic water containing 50 mg P/L, pH 7 for 360 min. At the same condition, phosphate removal efficiency of the NaOH-treated hydrochar, the Ca-, Mg- and Fe-modified hydrochars were 52, 58, 62 and 82 %. More than 98 % of phosphorus were removed by hydrochars loaded with Ca, Mg and Fe when adsorbent dosage increased from 2 g/L to 20 g/L. The adsorption capacity of the Ca-, Mg- and Fe-modified hydrochars increased from 12.3, 12.5 and 19.0 mg/g to 30.5, 34.9 and 40.8 mg/g when the initial phosphate concentrations increased from 50 mg P/L to 100 mg P/L. This study proposed an efficient method for conversion of cassava stem, one of the abundant agricultural solid wastes, into promising adsorbents that can be used for phosphorus removal and recovery from water and wastewater. It is worth noting that the benefits and limitations of using spent hydrochar which has high phosphorus and other salt contents as a replacement for chemical fertilizer should be further investigated.

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