

RESEARCH ARTICLE

Ammonia and phosphorus removal from agricultural runoff using cash crop waste-derived biochars

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HIGHLIGHTS

- Orange tree residuals biochar had a better ability to adsorb ammonia.
- Modified tea tree residuals biochar had a stronger ability to remove phosphorus.
- Partially-modified biochar could remove ammonia and phosphorus at the same time.
- The real runoff experiment showed an ammonia nitrogen removal rate of about 80%.
- The removal rate of total phosphorus in real runoff experiment was about 95%.

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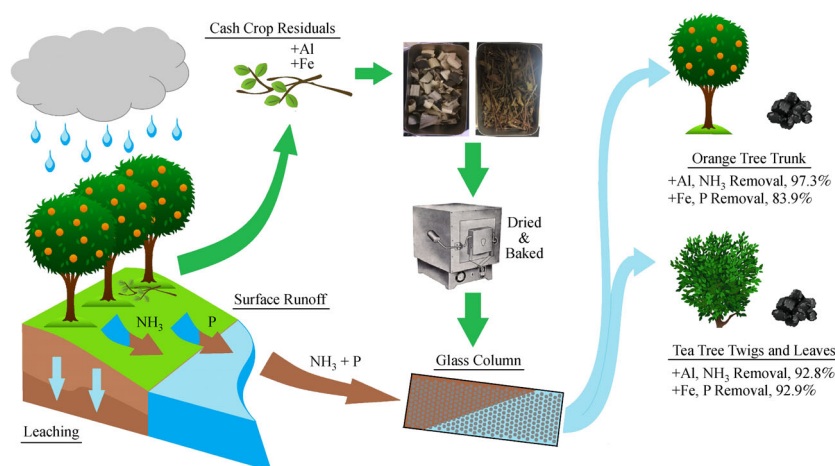
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GRAPHIC ABSTRACT



ABSTRACT

Adsorption of biochars (BC) produced from cash crop residuals is an economical and practical technology for removing nutrients from agricultural runoff. In this study, BC made of orange tree trunks and tea tree twigs from the Laoguanhe Basin were produced and modified by aluminum chloride (Al-modified) and ferric sulfate solutions (Fe-modified) under various pyrolysis temperatures (200°C–600°C) and residence times (2–5 h). All produced and modified BC were further analyzed for their abilities to adsorb ammonia and phosphorus with initial concentrations of 10–40 mg/L and 4–12 mg/L, respectively. Fe-modified Tea Tree BC 2h/400°C showed the highest phosphorus adsorption capacity of 0.56 mg/g. Al-modified Orange Tree BC 3h/500°C showed the best performance for ammonia removal with an adsorption capacity of 1.72 mg/g. FTIR characterization showed that P = O bonds were formed after the adsorption of phosphorus by modified BC, N-H bonds were formed after ammonia adsorption. XPS analysis revealed that the key process of ammonia adsorption was the ion exchange between K^+ and NH_4^+ . Phosphorus adsorption was related to oxidation and interaction between PO_4^{3-} and Fe^{3+} . According to XRD results, ammonia was found in the form of potassium amide, while phosphorus was found in the form of iron hydrogen phosphates. The sorption isotherms showed that the Freundlich equation fits better for phosphorus adsorption, while the Langmuir equation fits better for ammonia adsorption. The simulated runoff infiltration experiment showed that 97.3% of ammonia was removed by Al-modified Orange tree BC 3h/500°C, and 92.9% of phosphorus was removed by Fe-modified Tea tree BC 2h/400°C.

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1 Introduction

In China, various agricultural chemicals, such as fertilizers, pesticides, and herbicides, are being used to increase the output of crops (Xu et al., 1992). Of great concern is the

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risk posed by the contamination of water with excessively dosed phosphorus and nitrogen from agricultural runoff (Carpenter et al., 1998). As rainwater travels over impervious surfaces, nutrients are washed into bodies of water and leading to eutrophication (Ansari and Gill, 2011). Groundwater becomes contaminated when rainwater penetrates the ground and carries down the pollutants (Conrad et al., 1992). Eutrophication in lakes, reservoirs, estuaries, and rivers is widespread all over the world, especially in developing countries like China (Yang et al., 2008). The Laoguanhe River is an important water source conservation area in the upstream of the Middle Route of the South-to-North Water Diversion Project (Sun et al., 2016). 13.4% of the Laoguanhe Basin is under high to highest risk of agricultural non-point source pollution, and a majority of the zone with the high risk of agricultural non-point source pollution belongs to the cash crop cultivating area (Wang et al., 2010).

The cash crop is an agricultural crop, cultivated for sale to return a profit (Fafchamps, 1992). Disposal of agricultural residuals, including cash crop waste, poses significant economic and environmental problems (Yao et al., 2011). Among a multitude of agricultural residuals disposal methods, the production of biochars (BC) derived from agricultural waste in a pyrolysis process (Lehmann and Stephen, 2009) is gaining an increasing interest (Srinivasan et al., 2015). BC is not only an effective method to reuse local cash crop waste, but it can also be applied in situ to remove nutrients from agricultural runoff and protect the local water environment.

Traditional technologies of removing nitrogen and phosphorus from polluted water or wastewater are always applied in separate processes. Precipitation through metals or Enhanced Biological Phosphorous Removal (EBPR) was frequently used for phosphorus removal (Barker and Dold, 1996) while biological nitrogen removal processes and stripping (Zhang et al., 2008) were used for ammonia removal. It will increase the difficulty in operation and maintenance if the multi-processes are applied in treating agricultural runoff. In comparison, adsorption can be used as a universal method to remove nutrients from agricultural runoff (Liu et al., 2015). Although traditional adsorbents used for nutrients removal from water are expensive (Chen et al., 2011), BC is a cheap adsorbent (Inyang et al., 2012) that can be used as an alternative sorbent to remove aqueous chemical contaminants (Zhang et al., 2015). BC derived from corn straw proved to be useful for the removal of nutrients, heavy metals, and the amelioration of soil (Chi et al., 2017).

BC's characteristics strongly depend on the raw material from which they are made (Sun et al., 2012). Raw material affects its ability to adsorb various pollutants. BC produced from olive husks, and forest waste was able to remove phenanthrene and six heavy metals in a column experiment (Piscitelli et al., 2018). BC produced from corn straw adsorbed 99.24% of Cd and 98.62% of Pb from water (Chi

et al., 2017). Multiple organic contaminants (e.g., 99% of influent atrazine and 90% of influent fipronil) can be removed by woodchip-BC (Ashoori et al., 2019). In addition, particle size, pyrolysis temperature, and residence time also have significant effects on BC composition, pore structure, and adsorption ability (Doydora et al., 2011). A higher pyrolysis temperature of the magnetic nitrogen-doped sludge BC resulted in a higher graphitic degree and more abundant graphitic carbon (Yu et al., 2019). Corn cob derived BC produced by pyrolysis at 400°C had higher adsorption capacity than those produced at 600°C as adsorbents for ammonium-nitrogen removal from an aqueous solution (Zhang et al., 2014).

A large number of studies on BC were carried out recently. It was observed that non-modified BC had strong potential for adsorbing ammonia from water, whereas absorbing phosphorus was proven to be ineffective (Sarkhot et al., 2013). Pine-feedstock BC has a strong ability to remove phosphorus, but a weaker ability for nitrogen removal (Coleman et al., 2019). The non-modified mixed hardwood shavings BC prepared at 300°C has adsorbed 79% of ammonia and 60% of phosphorus (Xie et al., 2015). MgO wood chip BC was able to remove 17.5% to 36.4% of ammonia and 4.1% to 19.7% of phosphorus (Xie et al., 2015). Additionally, it was also found that 66% of ammonia can be adsorbed by non-modified peanut hull derived BC produced at 600°C, but it released about 97% of phosphorus to the water (Chen et al., 2011). Orange peel (OP) BC modified by iron (FeO) and magnetic modified (MOP) and produced at 250°C removed phosphorus with the efficiency of 67% (MOP250°C), 7% (OP250°C), 70% (FeO250°C) (Chen et al., 2011). Different modification materials and methods were researched to improve the removal efficiency of target pollutants. Various modification methods of municipal sewage sludge (MS) derived BC were used by (Tang et al., 2018) for antibiotics removal, and the best adsorption capacity was obtained from alkali-acid combined modification of MS BC produced at 800°C. Fe-modified BC showed high efficiency for phosphorus removal (Liu et al., 2015). Al-modified BC improved arsenic removal from synthetic urban runoff (Liu et al., 2019). Even though many types of BC produced from various residuals were tested for an ability to remove pollutants from the water, the observed results did not provide a clear understanding of the ability of agricultural waste-derived BC to remove nutrients from rainwater runoff.

In this study, Fe-modified, Al-modified, and non-modified BC produced from two typical local cash crops residues of Orange and Tea Tree were compared for their abilities to remove ammonia and phosphorus from agricultural runoff in the Laoguanhe river basin. The aim of this study was to determine the effects of raw materials, BC modification reagents, and production conditions on the ability of BC to adsorb ammonia and phosphorus from

the water and the potential inherent mechanisms. The findings of this study are proposing an economical and effective strategy for mitigating agricultural runoff pollution and simultaneously disposing of agricultural waste in the Laoguanhe Basin.

2 Materials and methods

2.1 BC production and modification

Orange tree trunks and tea tree twigs with leaves were gathered from the Laoguanhe River Valley in Xichuan County, Henan Province, China. They were used to produce Orange Tree BC and Tea Tree BC.

Orange tree trunks were chopped into 2–4 cm long blocks. Tea tree twigs were cropped to sizes varying from 5–15 cm in length and 2–5 mm in thickness. These twig pieces, along with the leaves attached to them, were used together to prepare the Tea Tree BC.

Both types of raw material were oven-dried at 70°C for 12 h, then placed in a metallic container sealed with aluminum foil. These pieces underwent the process of slow pyrolysis in a muffle furnace (TNQ1100-40, Shanghai Shinbae Industrial Co., Ltd.), at different temperatures (300°C, 400°C, 500°C, 600°C) and residence times (2 h, 3 h, 4 h, 5 h). The furnace was set to gradually rise in temperature of 10°C each minute until it reached the necessary temperature and then cooled down to room temperature.

Conducting this production sequence, a total of 32 non-modified BC were produced. BC samples were crumbled into granulated particles with a diameter of 1 mm. In the following experiments, only crumbled BC samples were used.

To execute the modifications, aluminum chloride (AlCl_3) and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were selected as additive agents due to the high reactivity of metals in contact with phosphorus. For modifying, the 200 g of the raw material was soaked for 1 h in 1 mol/L aluminum chloride solution and dried for 24 h at 25°C before it was inserted into the muffle furnace. For the modification with ferrous sulfate, the same procedure was carried out. A total of 64 modified BC samples (32 Orange Tree BC and 32 Tea Tree BC) were produced.

2.2 Ammonia and phosphorus adsorption

Of each sample, 1 g of granulated BC was mixed with 100 mL of ammonia solutions with concentrations of 10 mg/L, 20 mg/L, and 40 mg/L in a 100 mL flask; the same amount of BC was added to 100 mL of phosphorus solutions with concentrations of 4 mg/L, 8 mg/L, and 12 mg/L. Then the sample flasks were oscillated at 25°C, 120 r/min within 24 h for ammonia samples and 1 h for phosphorus samples in the oscillator (DHG 9070A,

Shanghai Jinghong Laboratory Instrument Co., Ltd.), 10 mL of each sample were collected from the flasks after 1, 2, 3, 6, 12, 24 h and after 5, 10, 20, 30, 45, and 60 min. All samples were filtered through a 0.45 μm filter for further analysis.

The ammonia concentrations were measured by the salicylic acid spectrophotometry method (HJ 536-2009) with a spectrophotometer (DR 6000™ UV-VIS, HACH, USA) with the wavelength for Nitrogen set at 697 nm. The phosphorus concentration was measured via the malachite green-molybdous phosphate method using a spectrophotometer (DR 6000™ UV-VIS, HACH, USA) with the wavelength for phosphorus set at 700 nm (Liu et al., 2015). The adsorption was measured by means of the photo-colorimetric method. The spectrophotometer adsorption level was determined by the light-absorption measurement.

A total of 96 samples (48 Orange Tree BC and 48 Tea Tree BC) were examined for ammonia and phosphorus removal efficiency.

For calculating the adsorption value at the solid adsorbent-solution boundary, the empirical equation of Freundlich was used:

$$q = K \cdot C^{1/n} \quad (1)$$

where q is adsorption of ammonia and phosphorus (mg/g), C is adsorbent equilibrium concentration (mg/L), K is adsorption constant (mg/g)·(L/mg), and $1/n$ is dimensionless strength of adsorption (Scheidegger and Sparks, 1996).

Langmuir created and substantiated the theory of monomolecular adsorption of gases by solid adsorbents, assuming that, active centers homogeneously distributed on the surface. The adsorption is localized, and its isotherm equation was calculated by a formula:

$$q = \frac{bQC}{1 + Cb} \quad (2)$$

where q is specific adsorption (mg/g), Q is limiting adsorption (mg/g) and b is an adsorption constant (L/mg) (Chiou, 2002).

2.3 BC characteristics

Of each sample, 1g of BC was mixed with 100 mL phosphorus solution and 100 mL ammonia solution in a 100 mL flask and oscillated at 25°C for 24 h at 120 r/min in the oscillator. Then, it was separated from the water and oven-dried at 105°C.

To analyze BC microstructure and surface characteristics, samples were examined by means of scanning electron microscopy (SEM) (Carl Zeiss, Merlin, GEMINI). For SEM, the microscope investigation provided high-resolution images that clearly revealed samples' detailed pores structure. The elemental chemical composition

information was generated by the software INCA, Oxford Instruments.

Fourier Transform Infrared (FTIR) Nicolet 6700 (Thermo Fisher Scientific, Massachusetts, USA) was used to obtain the infrared spectrum of absorption. The spectra were recorded in KBr at 4 cm^{-1} resolutions.

X-ray diffractometer XRD (D8 ADVANCE, Bruker Corporation, Massachusetts, USA) was used for identifying the chemical bonds and crystallographic structure of BC samples.

X-ray photoelectron spectroscopy (XPS) (EscaLab 250Xi, Thermo UK) was used to analyze the surface chemistry of BC samples in its initial state and after ammonia and phosphorus adsorption.

2.4 Simulated runoff infiltration experiment

Four glass columns with a thickness of 1.5 mm, a length of 50 cm, and an internal diameter of 4 cm were used for the leaching column test. Each column was packed with 100 g of BC. Four types of BC samples were used for this experiment. 100 g of Tea Tree BC sample occupied 50 cm of the column, while 100 g of Orange Tree BC sample occupied around 30 cm of the column. Artificial rainwater was prepared for this experiment using distilled water from the campus of Tsinghua University, potassium dihydrogen phosphate, and ammonium chloride so that the concentration of ammonia nitrogen and phosphorus in the self-dispersing water were about 1 and 0.5 mg/L, respectively.

Al-modified Orange Tree BC 3h/500°C and non-modified Tea Tree BC 3h/400°C were selected as the most efficient in ammonia removal among 96 BC samples from the described above experiments. Al-modified Orange Tree BC 3h/500°C and Fe-modified Tea Tree BC 2h/400°C were selected as the most efficient in phosphorus removal. The selected samples were used in the simulated runoff infiltration experiment. Rainwater with NH_4^+ a concentration of 1.11 mg/L and PO_4^{3-} , and a concentration of 0.56 mg/L was used in a total volume of 45.0 L for each column. Every 500 mL of runoff water leached from the column was tested. The adsorption hydraulic retention time (HRT) was 6–10 h.

3 Results and discussion

3.1 BC properties

An SEM made the pore structure of modified and non-modified BC samples clearly visible (Fig. 1). Non-modified BC samples' pores were clean (Fig. 1(a)), while modified BC samples' pores were laden with altering agents (Fig. 1(b)). Pores of Orange Tree BC were relatively small and dense compared to Tea Tree BC (Fig. 1(c)). While aluminum used for the modification of Orange Tree BC was mostly found inside the pores, iron used for the

modification of Tea Tree BC was mostly surrounding the surface of the pores (Fig. 1(b, e)). While the adsorbed ammonia and phosphorus were mostly found inside the pores of Orange Tree BC (Fig. 1(c)), Tea Tree BC was entirely covered by adsorbed phosphorus (Fig. 1(d)). The bright zones on the negative picture (Fig. 1(f)) indicated metallic formations (Reimer, 1998).

3.1.1 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the starting BC revealed a weak difference with those obtained for BC with adsorbed ammonia ions (Fig. 2), probably corresponding to NH_4^+ . In the region of $3600\text{--}3000\text{ cm}^{-1}$, where the stretching bands of N-H were expected, two weak small peaks at 3100 and 3415 were observed. N-H bands were overlapped by the water O-H bonds, and the correct identification was hardly available. Although, when comparing the Al-modified Orange Tree BC before and after ammonia adsorption, the second spectrum had lower transmittance in the region.

The IR spectra of BC after phosphorus removal revealed distinct absorption bands. The Al-modified Orange Tree BC 3h/500°C showed a peak at 1036 cm^{-1} representing P = O band stretching after phosphorus was adsorbed, (Fig. 2(a)). A new peak of $1090\text{--}1030\text{ cm}^{-1}$ appeared after phosphorus adsorption, represented by H_2PO_4^- (Wu, 1994). These changes in the peak intensity and the formation of new peaks showed the ability of Al-modified Orange Tree BC 3h/500°C to adsorb phosphorus. The binding of phosphate to the metal oxide surface was difficult to predict in detail due to the interplay between protonated surface species and hydrogen bonding (Zheng et al., 2012).

In the spectrum of Fe-modified Tea Tree BC 2h/400°C loaded with phosphorus, the 1203 cm^{-1} band has risen (Fig. 2(b)), indicating the P = O stretching represented by phosphine acid (RO) $\text{H}_2\text{P} = \text{O}$, $\text{R}_2\text{P} = \text{O}$, or $\text{RHP} = \text{O}$ ($1220\text{--}1180\text{ cm}^{-1}$), (Wu, 1994).

3.1.2 XPS analysis

The elements' relative concentrations (atomic mass %) analysis showed that the quantity of nitrogen in 1g of BC sample (wetted for 24 h) had increased compared to the initial quantity before the ammonia adsorption (Fig. 3), verifying the adsorption of nitrogen.

The relative concentrations of other elements were changing, too, as suggested by the decrease of C and the increase of O (Fig. 3(b)). Possibly, it happened as a result of the interaction of C, H, and O, existent in the BC and solutions H_2O , owing to the formation of bonds with oxygen and soluble bonds with C, which was left in the solution. As distinct from modified Orange Tree BC, modified Tea Tree BC did not show that the nitrogen was adsorbed. The discharge of nitrogen occurred while the

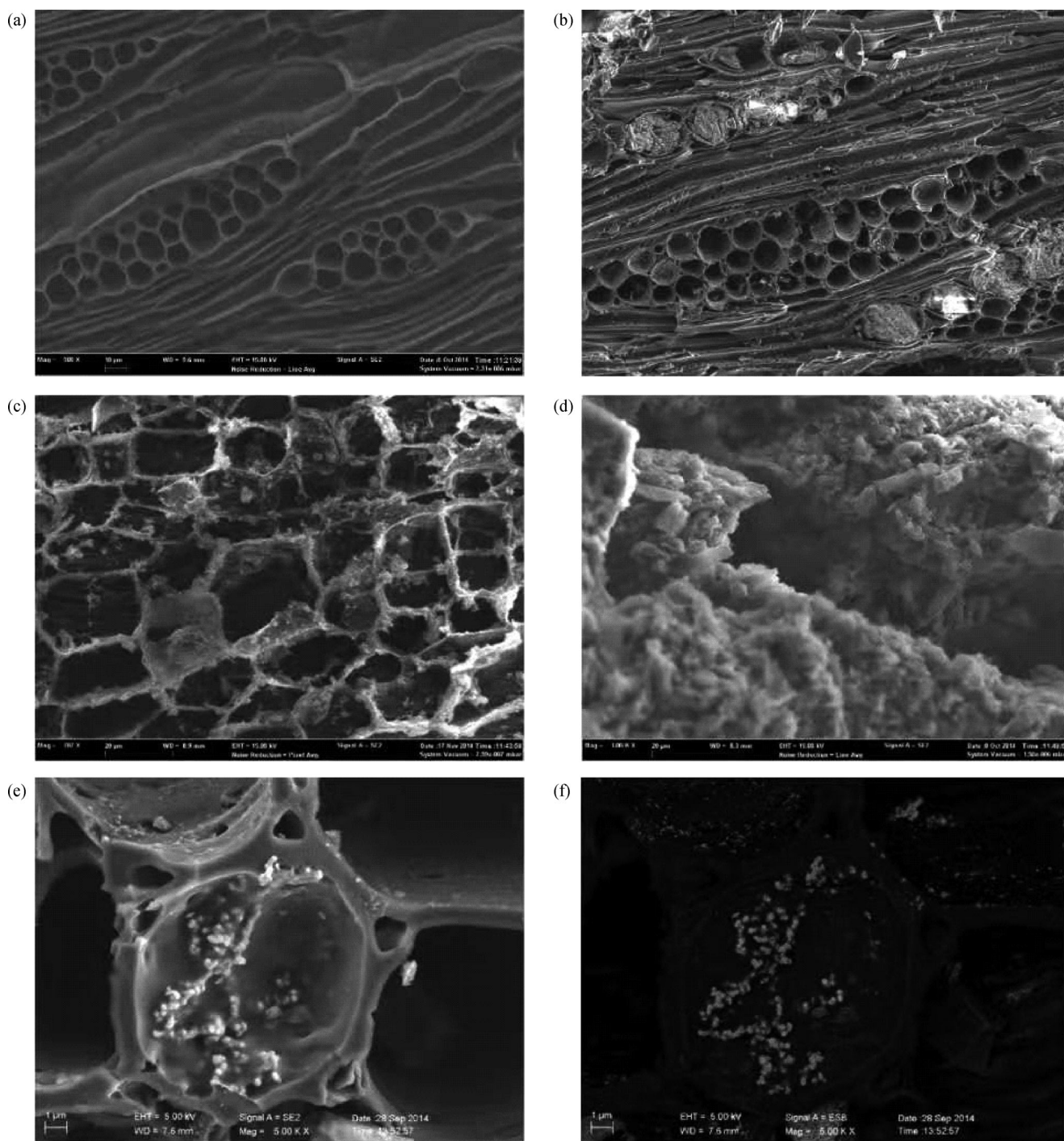


Fig. 1 SEM image of: (a) non-modified Orange Tree BC, (b) Al-modified Orange Tree BC after adsorption of phosphorus, (c) Fe-modified Tea Tree BC before phosphorus adsorption, (d) Fe-modified Tea Tree BC after phosphorus adsorption, (e) Al-modified Orange tree BC before adsorption, (f) Al-modified Orange tree BC before adsorption negative color image.

concentration of potassium was decreasing (Fig. 3(a)).

The reduction of K, which was observed while the concentration of nitrogen increased, allowed us to assume that ion exchange occurred between NH_4^+ and K^+ on the BC surface and represented the adsorption mechanism. In this way, potassium can be determined as the cause of the nitrogen adsorption by BC.

From the elements' relative concentrations (atomic %) analysis before and after phosphorus adsorption, it was observed that the quantity of phosphorus in the BC increased in contrast with the initial (Fig. 3(a)), verifying the adsorption of phosphorus by BC. There are visible interactions between PO_4^{3-} and Fe^{3+} . Interaction of C, H, and O, existent in the BC, occurred because of the

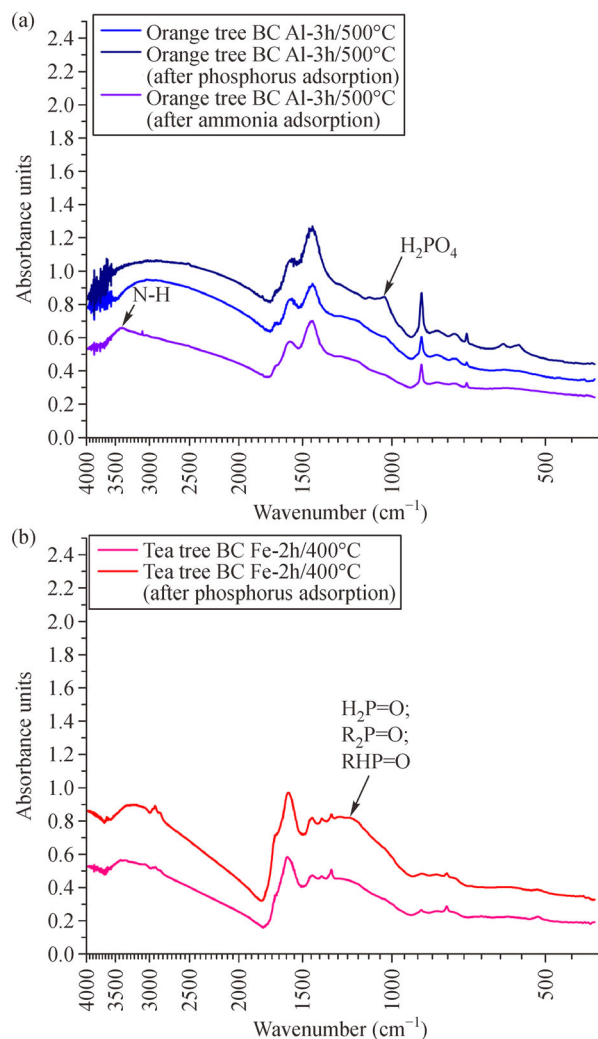


Fig. 2 FTIR spectrum of (a) Al-modified Orange Tree BC 3h/500°C before and after the adsorption of ammonia and phosphorus, (b) Fe-modified Tea Tree BC 2h/400°C before and after the adsorption of phosphorus.

formation of bonds with oxygen (e.g., $\text{Fe}(\text{OH})_3$, which remained on the BC) and soluble bonds with carbon (Singhs et al., 2017).

Both modified and non-modified Tea Tree BC adsorbed phosphorus, though the latter adsorbed insignificant quantities. For Orange Tree BC, only modified BC adsorbed phosphorus, which can be observed by the increasing atomic fraction.

3.1.3 XRD analysis

The structures of non-modified Orange Tree BC 3h/500°C and Al-modified Orange Tree BC 3h/500°C were very similar (Fig. 4(a)); however, in the spectrum of Al-modified Orange Tree BC 3h/500°C the peak located in the proximity of 24° provided evidence of modification. This

peak, according to the library of Jade 2.0, was represented by aluminum phosphate. The spectrum of Al-modified Orange Tree BC 3h/500°C loaded with ammonia, new peaks have shaped at 23° and 25° , and probably these were new formations of potassium aluminum amide imide. The spectrum of non-modified Orange Tree BC 5h/400°C loaded with ammonia (Fig. 4(b)) revealed new peaks at 27° and 28° , which also reflected the presence of potassium nitrate. Non-modified Tea Tree BC 3h/400°C loaded with ammonia compare to non-modified Tea Tree BC 3h/400°C before adsorption had a new peak at 36° , signifying calcium nitrate chloride and potassium nitrate (Fig. 4(d)).

The peak related to Al-modified Orange Tree BC 3h/500°C loaded with phosphorus, has risen at 25° (Fig. 4(a)), and corresponded to phosphine and phosphorus chloride. In the spectra of Fe-modified Tea Tree BC 2h/400°C, peaks have appeared at 15° , 24° , 30° , 36° and 38° (Fig. 4(c)). These peaks indicated the iron hydrogen phosphate hydrate or iron hydrogen phosphate. The comparison of Fe-modified Tea Tree BC 2h/400°C before adsorption and Fe-modified Tea Tree BC 2h/400°C loaded with phosphorus, revealed that new peaks have emerged at 17.5° , 37.4° , 53.5° , 57° and 62.5° (Fig. 4(c)), coinciding with the absorption bands of iron oxide, hydrogen phosphate, and iron chloride hydrate.

3.2 Ammonia and phosphorus removal

All the produced BC samples were tested on its ability to remove ammonia and phosphorus from the water. Initial concentrations of ammonia were 10 mg/L, 20 mg/L and 40 mg/L, initial concentrations of phosphorus were 4 mg/L, 8 mg/L and 12 mg/L (Table 1). Adsorption efficiencies for all BC samples are represented in (Fig. 5) with initial concentrations 10 mg/L for ammonia and 4 mg/L for phosphorus. Only the best performance BC efficiencies were shown for all three initial concentrations (Fig. 6).

3.2.1 Effect of production temperatures and durations on BC adsorption capacity

Orange Tree BC and Tea Tree BC were produced using different residence times and pyrolysis temperatures. For ammonia removal, Orange Tree BC samples had about two times more efficient than Tea Tree BC. Non-modified and Al-modified Orange Tree BC samples produced at 400°C and 500°C showed a higher adsorption capacity than Orange Tree BC samples produced at 300°C and 600°C (Table 1(a)). Orange Tree BC produced at 400°C and 500°C within 4 h showed the most optimal results. Fe-modified Orange Tree BC showed the lowest adsorption capacity.

For phosphorus removal, among all BC samples, only Fe-modified Tea Tree BC showed a reasonable ability to

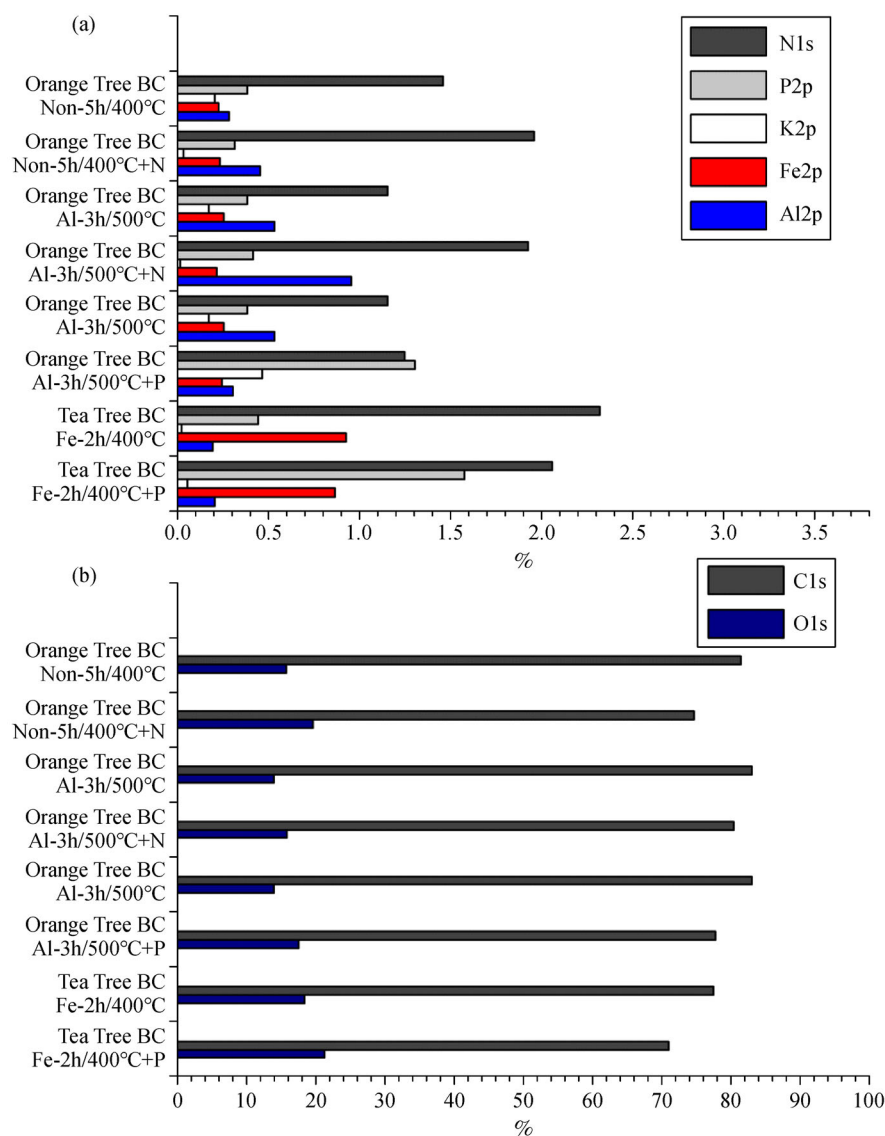


Fig. 3 Atomic mass percentage of chosen BC elemental composition before and after the adsorption of ammonia and phosphorus (a) N, P, K, Fe, Al, (b) O, C.

adsorb phosphorus, and BC produced at 400°C and 500°C pyrolysis temperatures within 4 h showed the highest adsorption capacities compared to those produced at 300°C and 600°C. Production duration of 2h was found to be most optimal for 400°C pyrolysis of Fe-modified Tea Tree BC, 4h production time was most optimal for 500°C pyrolysis of Fe-modified Tea Tree BC (Table 1(b)). Among Orange Tree BC samples, only Al-modified Orange Tree BC produced at 400°C and 500°C pyrolysis showed a weak ability for phosphorus adsorption.

3.2.2 Ammonia removal

It was demonstrated that Orange Tree BC has a strong ability to remove ammonia from water (Fig. 5(a)). On the

efficiency scale, the most efficient were non-modified Orange Tree BC 5h/400°C and Al-modified Orange Tree BC 3h/500°C with the highest adsorption efficiencies at 65.5% and 65.2, respectively (Fig. 6(a)).

Among Tea Tree BC samples, non-modified Tea Tree BC 3h/400°C showed the highest ammonia adsorption efficiency of 32.4% (Fig. 6(a)). Only non-modified Tea Tree BC was able to remove ammonia, while modified Tea Tree BC was found lacking this capability (Fig. 5(b)).

It was concluded that Orange Tree BC removes ammonia three times better than Tea Tree BC. Furthermore, both modified and non-modified Orange Tree BC can remove ammonia. In this case, the orange tree has proven to be a suitable material for producing BC and removing ammonia from the water.

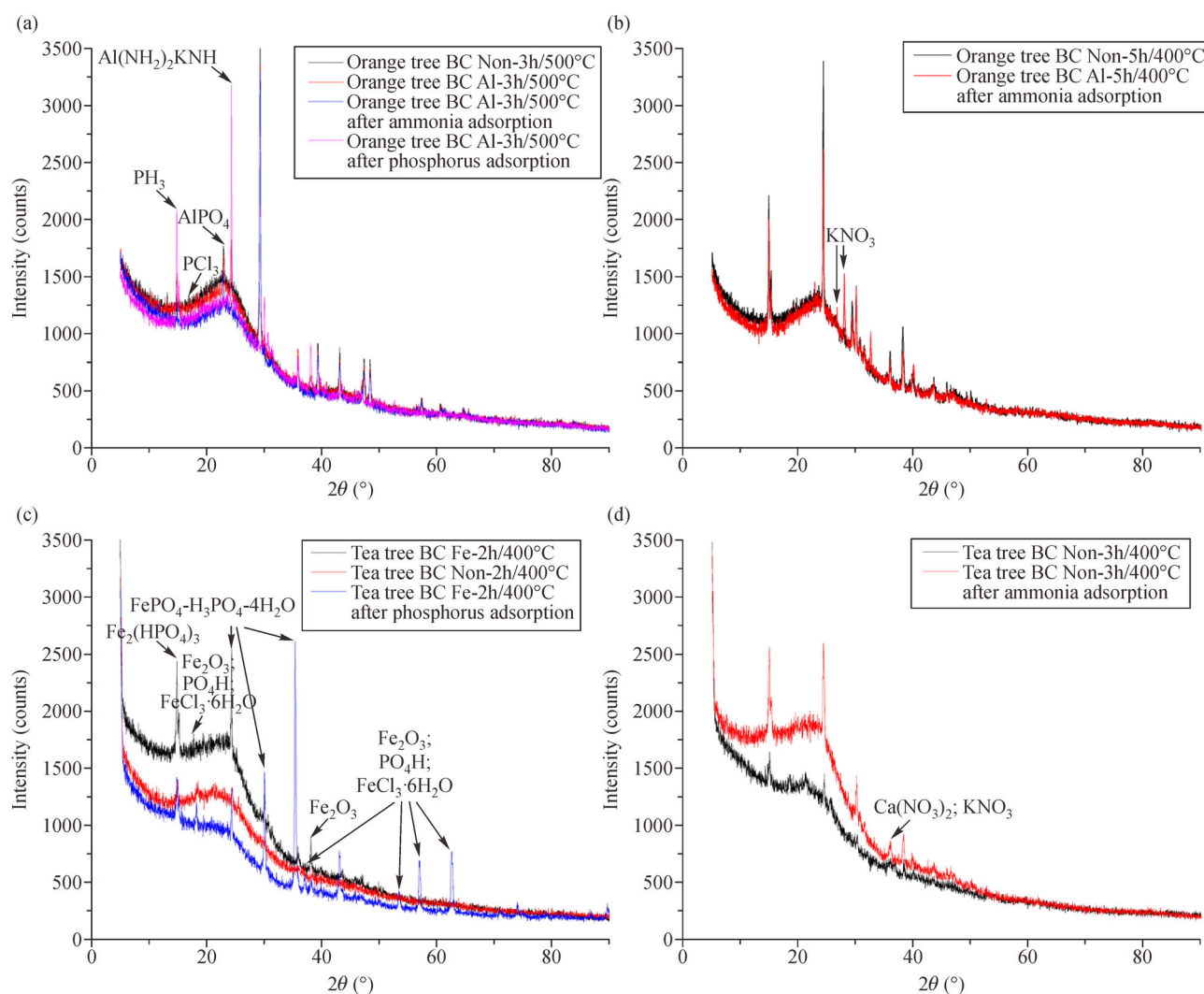


Fig. 4 XRD comparison of (a) Non-modified Orange Tree BC 3h/500°C and Al-modified OTBC 3h/500°C before and after phosphorus adsorption, (b) of Non-modified Orange Tree BC 5h/400°C before and after ammonia adsorption, (c) Non-modified Tea Tree BC 2h/400°C and Fe-modified Tea Tree BC before and after phosphorus adsorption, (d) Non-modified Tea Tree BC 3h/400°C before and after ammonia adsorption.

While none of the modified Tea Tree BC adsorbs ammonia, Al-modified Orange Tree BC has registered the best result among Orange Tree BC samples. Typically, modified BC cannot remove ammonia. While Tea Tree BC samples acted usually, the samples Al- and Fe-modified Orange Tree BC were found to be able to remove ammonia. Tea tree residuals were relatively small; however, the pieces of orange tree trunk used for BC preparation were relatively large. Although the tea tree residuals were entirely saturated by the modifying solution, the trunks of the orange trees were not wholly saturated during the modification process, and only the surface was saturated while the inner part of the bricks was left untouched. When ground, the mixture of the Orange Tree BC sample included half-modified particles from the inner portion of the sample. The same conclusion could be drawn in relation to iron-modified samples.

Therefore, the capacity of Al-modified Orange Tree BC and Fe-modified Orange Tree BC to adsorb ammonia may be due to the non-modified part of the BC reaction with ammonia ions. This could be beneficial to the large-scale production of BC. This type of half-modified BC can be applied for both ammonia and phosphorus removal at the same time.

3.2.3 Phosphorus removal

For phosphorus removal, we determined that the production temperature influenced BC structure and adsorption characteristics to a great extent. BC produced at 400°C, and 500°C has exhibited the best results (Fig. 5). Neither non-modified nor Fe-modified Orange Tree BC has shown an ability to remove phosphorus from water. Al-modified

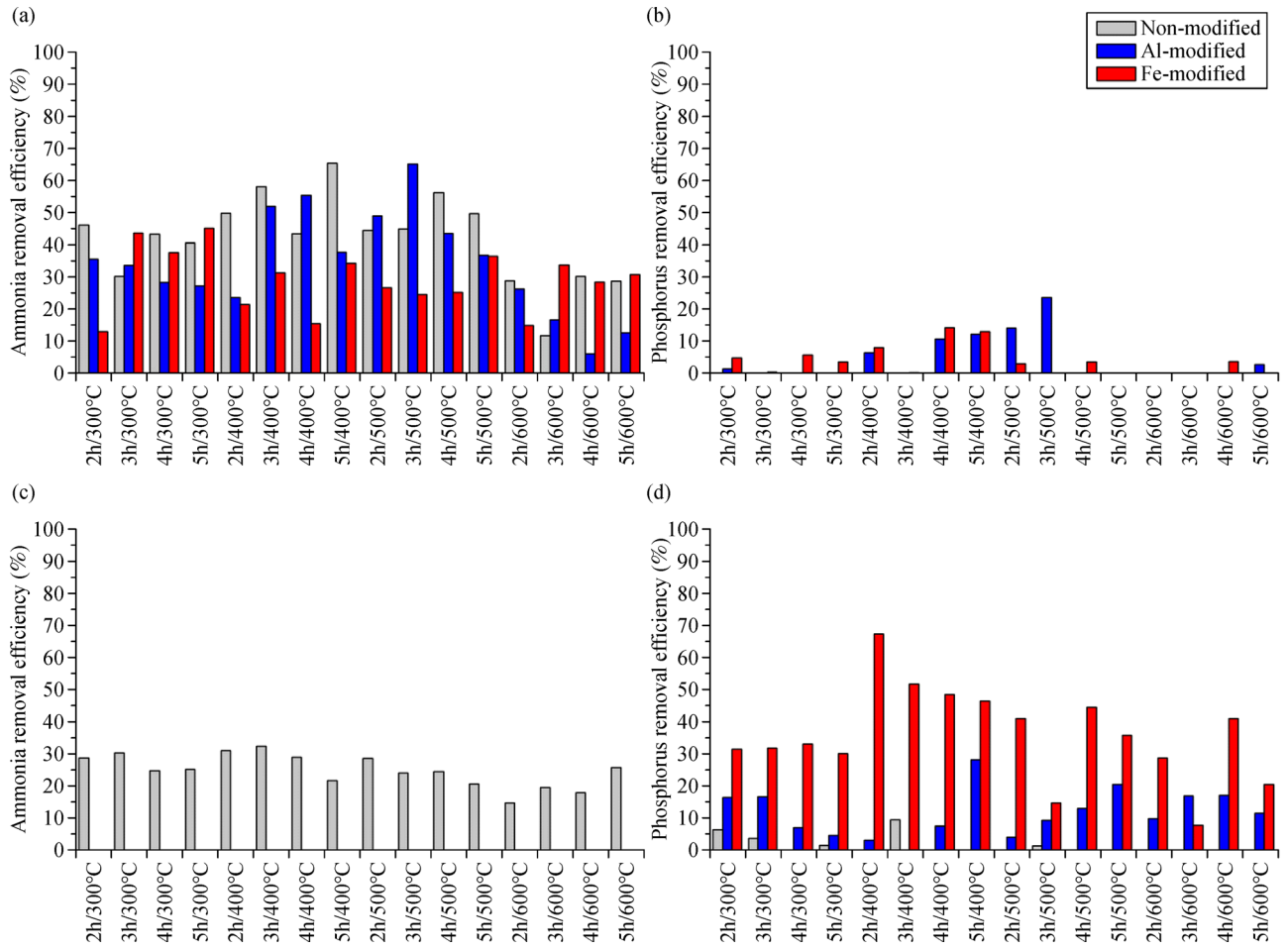


Fig. 5 Removal efficiency of (a) Orange Tree BC after ammonia adsorption, (b) Orange Tree BC after phosphorus adsorption, (c) Tea Tree BC after ammonia adsorption, (d) Tea Tree BC after phosphorus adsorption.

samples, prepared at 400°C–500°C, have shown inconsistent results for phosphorus adsorption (Fig. 5(c)). Al-modified Orange Tree BC 3h/500°C samples, among other Orange Tree BC, shows the highest sorption efficiency rate

of 23.7% (Fig. 6(b)), which is about three times lower than the same index for Tea Tree BC. Fe-modified Tea Tree BC 2h/400°C showed the best phosphorus adsorption result among all BC samples with an efficiency rate of 67.2%

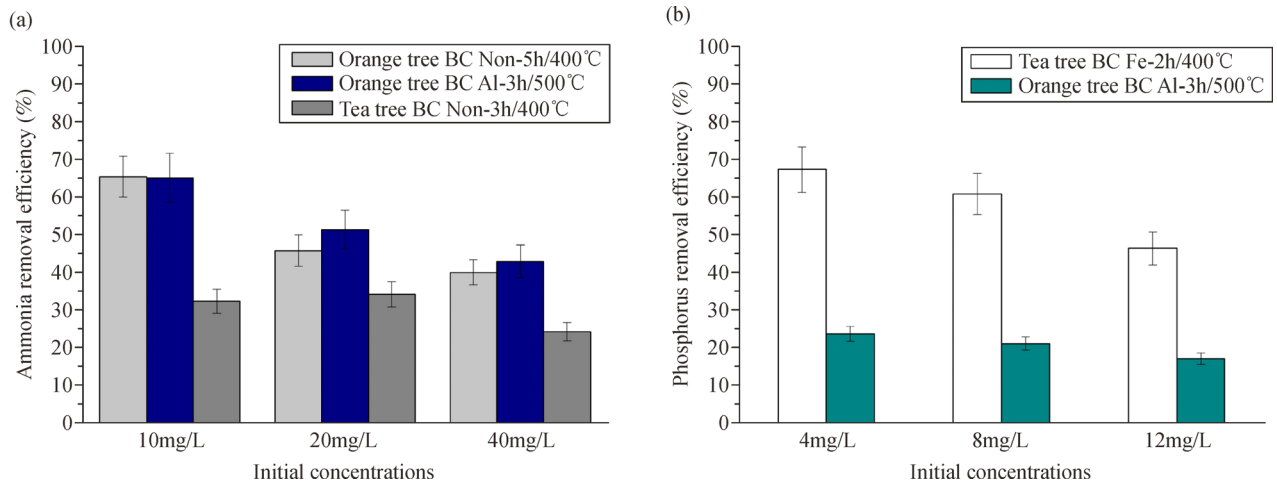


Fig. 6 The best performance BC in (a) ammonia adsorption, (b) phosphorus adsorption.

Table 1 Ammonia and phosphorus adsorption capacity of all BC samples (mg/g)

(a) Ammonia adsorption capacity

Initial conc.	Temp. duration	300°C			400°C			500°C			600°C		
		a)	b)	c)	a)	b)	c)	a)	b)	c)	a)	b)	c)
10 mg/L	2h	0.46	0.36	0.13	0.50	0.24	0.22	0.45	0.49	0.27	0.29	0.26	0.15
	3h	0.30	0.34	0.44	0.58	0.52	0.32	0.45	0.65	0.25	0.12	0.17	0.34
	4h	0.43	0.28	0.38	0.44	0.56	0.16	0.56	0.44	0.25	0.30	0.06	0.29
	5h	0.41	0.27	0.45	0.66	0.38	0.34	0.50	0.37	0.37	0.29	0.13	0.31
20 mg/L	2h	0.83	0.45	0.28	1.08	0.37	0.49	0.90	0.89	0.74	0.47	0.49	0.49
	3h	0.63	0.53	0.72	1.00	0.84	0.64	0.74	1.03	0.58	0.26	0.38	0.67
	4h	0.85	0.47	0.52	0.91	0.76	0.33	0.99	0.70	0.33	0.55	0.14	0.33
	5h	0.87	0.59	0.56	0.92	0.47	0.53	0.80	0.54	0.46	0.40	0.31	0.45
40 mg/L	2h	1.26	0.63	0.36	1.47	0.49	0.76	1.40	1.49	1.14	0.86	0.58	1.15
	3h	0.85	0.85	1.01	1.54	1.51	0.94	1.15	1.72	0.88	0.58	0.63	0.96
	4h	1.43	0.72	0.70	1.48	1.32	0.52	1.56	1.21	0.55	1.00	0.43	0.57
	5h	1.42	1.21	0.92	1.60	1.04	0.86	1.02	0.68	0.85	0.41	0.75	0.83

(b) Phosphorus adsorption capacity

Initial conc.	Temp. duration	300°C			400°C			500°C			600°C		
		d)	e)	f)	d)	e)	f)	d)	e)	f)	d)	e)	f)
4 mg/L	2h	0.03	0.07	0.13	0.00	0.01	0.27	0.00	0.02	0.16	0.00	0.04	0.11
	3h	0.02	0.07	0.13	0.04	0.01	0.21	0.01	0.04	0.06	0.00	0.07	0.03
	4h	0.00	0.03	0.13	0.00	0.03	0.19	0.00	0.05	0.18	0.00	0.07	0.16
	5h	0.01	0.02	0.12	0.00	0.11	0.19	0.00	0.08	0.14	0.00	0.05	0.08
8 mg/L	2h	0.02	0.07	0.13	0.00	0.03	0.49	0.00	0.04	0.18	0.00	0.10	0.12
	3h	0.02	0.10	0.14	0.05	0.01	0.37	0.01	0.06	0.08	0.00	0.10	0.06
	4h	0.00	0.03	0.14	0.00	0.03	0.35	0.00	0.07	0.20	0.00	0.10	0.18
	5h	0.01	0.04	0.12	0.00	0.12	0.29	0.02	0.09	0.22	0.00	0.07	0.09
12 mg/L	2h	0.02	0.07	0.14	0.00	0.05	0.56	0.00	0.06	0.20	0.00	0.12	0.12
	3h	0.03	0.17	0.16	0.06	0.00	0.42	0.02	0.10	0.09	0.01	0.14	0.08
	4h	0.00	0.03	0.16	0.00	0.03	0.41	0.00	0.07	0.31	0.00	0.11	0.20
	5h	0.00	0.06	0.13	0.00	0.13	0.35	0.03	0.10	0.26	0.00	0.07	0.10

Notes: a) Non-modified Orange Tree BC; b) Al-modified Orange Tree BC; c) Fe-modified Orange Tree BC; d) Non-modified Tea Tree BC; e) Al-modified Tea Tree BC; f) Fe-modified Tea Tree BC.

(Fig. 6(b)). Based on the observed results, it can be concluded that different modification agents are suitable only for certain types of raw materials. Iron BC modification showed a good phosphorus adsorption ability for Tea Tree but not for the Orange Tree. Overall, it can also be concluded that Tea Tree residuals were the more suitable raw material for phosphorus adsorption.

3.2.4 Adsorption isotherms

Experimentally, it was observed that the concentration of ammonium solution reached the equilibrium after 24h of oscillating mixing, while phosphorous solution reached its equilibrium concentration after 1h of oscillating mixing (Table 2). The constants of the Freundlich and Langmuir equations were calculated from the inclination and

intersection of straight lines in the corresponding coordinates of the linear equation. The calculated sorption capacity of ammonia was 1.72 mg/g; the sorption capacity of phosphorus was 0.56 mg/g.

Freundlich and Langmuir's equations revealed a strong convergence with the coefficients for phosphorus $R^2 = 0.977$ and $R^2 = 0.953$, but the Freundlich equation fits better than the Langmuir equation. Both Freundlich and Langmuir isotherm models revealed a good convergence with the coefficients for ammonia $R^2 = 0.98$ and $R^2 = 0.975$ (Table 3).

3.3 Simulated runoff infiltration experiment

The artificial rainwater samples were prepared and applied to the column filled with BC. Three BC samples that

Table 2 Ammonia and phosphorus adsorption kinetics by selected BC (mg/L)

(a) Ammonia removal speed by Orange Tree BC

Initial conc.(mg/L)	1 h	2 h	3 h	6 h	12 h	24 h	48 h
10.00	7.32	7.04	6.68	5.33	4.84	3.46	3.45
20.00	16.42	14.66	12.97	12.74	11.78	10.81	10.82
40.00	35.02	33.49	30.66	29.52	26.11	23.94	23.95

(b) Phosphorus removal speed by Tea Tree BC

Initial conc.	5 min	15 min	30 min	1 h	3 h	6 h	12 h
4.00	3.31	2.21	1.52	1.31	1.30	1.31	1.31
8.00	6.68	4.42	3.54	3.14	3.15	3.14	3.14
12.00	10.10	7.51	6.91	6.43	6.42	6.44	6.43

Table 3 Ammonia and phosphorus adsorption characteristics for the selected BC

BC sample	Langmuir equation			Freundlich equation		
	B (L/mg)	Q (mg/g)	R^2	K (mg/g)	n	R^2
Non-modified TTBC 3h/400 °C ^I	0.06	1.52	0.99	0.12	1.62	0.98
Al-modified Orange Tree BC 3h/500 °C ^I	0.22	1.77	0.98	2.66	2.24	0.98
Fe-modified Tea Tree 2h/400 °C ^{II}	0.96	0.58	0.95	0.25	2.15	0.98
Al-modified Tea Tree BC 3h/500 °C ^{II}	0.14	0.37	0.98	0.14	0.37	0.98

Notes: I. Ammonia adsorption by selected BC; II. Phosphorus adsorption by selected BC.

showed the best performance in the adsorption experiment were chosen for the simulated runoff infiltration experiment. Al-modified Orange Tree BC 3h/500°C and non-modified Tea Tree BC 3h/400°C were tested on ammonia removal capability, Al-modified Orange Tree BC 3h/500°C and Fe-modified Tea Tree BC 2h/400°C were tested on phosphorus removal capability.

The results in (Table 4) represented the mean value of influent and effluent concentrations after 90 operations. It has shown that Orange Tree BC was more effective than Tea Tree BC at removing ammonia; their effectiveness rates were equal to 97.3% and 92.8%, respectively. Orange Tree BC can be used as a strong ammonia adsorbent for runoff infiltration. On the other hand, Fe-modified Tea Tree BC 2h/400°C has proved to be more effective for phosphorus removal than Al-modified Orange Tree BC 3h/500°C with removal efficiencies of 92.9% and 83.9%, respectively. Fe-modified Tea Tree BC can be used as a strong phosphorus adsorbent for runoff infiltration. The combination of BC made of different agricultural residuals proved to be more effective for ammonia and phosphorus

removal from rainwater runoff, than BC made of one material, as their performance was different for target pollutants.

4 Conclusions

This research was dedicated to finding the most optimal BC made of local cash crop residuals for ammonia and phosphorus removal from agricultural runoff in the Laoguanhe basin area. It was observed that BC made of different materials have a different ability to remove ammonia and phosphorus from water. Orange Tree BC was found to be more effective for ammonium adsorption, while modified Tee Tree BC has a better ability to absorb phosphorus. For ammonia adsorption, the best results were obtained from non-modified Orange Tree BC 5h/400°C and Al-modified Orange Tree BC 3h/500°C with efficiency rate at 65.5% and 65.2%. Ammonia adsorption ability of Tea Tree BC was found to be relatively low, with the highest score obtained from non-modified Tea Tree BC

Table 4 Ammonia and phosphorus removal efficiency in the column leaching experiment

BC sample	Runoff volume (L)	Influent concentration (mg/L)	Effluent concentration (mg/L)	Removal efficiency (%)
Non-modified TTBC 3h/400 °C ^I	45	1.11	0.0	92.8
Al-modified Orange Tree BC 3h/500 °C ^I	45	1.11	0.03	97.3
Fe-modified Tea Tree 2h/400 °C ^{II}	45	0.56	0.04	92.9
Al-modified Tea Tree BC 3h/500 °C ^{II}	45	0.56	0.09	83.9

Notes: I. Ammonia adsorption by selected BC; II. Phosphorus adsorption by selected BC.

with an efficiency rate of 32.4%. In terms of phosphorus removal, the aluminum modification was observed to be more efficient for Orange Tree BC, while iron modification was found to be more suitable for Tea Tree BC. The best results were obtained from Fe-modified Tea Tree BC 2h/400°C with phosphorus adsorption of 5.6 mg/L with an efficiency rate of 67.3%. Orange Tree BC showed the highest phosphorus removal score was obtained by Al-modified Orange Tree BC 3h/500°C with an efficiency rate of 23.7%. The simulated runoff infiltration experiment showed above 90% of ammonia and phosphorus can be removed by a combination of Orange Tree BC and Fe-modified Tea Tree BC. The findings of this research are recommended for large-scale production and application of BC for nutrients removal from rainwater runoff.

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