Review

Evaluating biochar and its modifications for the removal of ammonium, nitrate, and phosphate in water

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ARTICLE INFO

ABSTRACT

Removal of nitrogen (N) and phosphorus (P) from water through the use of various sorbents is often considered an economically viable way for supplementing conventional methods. Biochar has been widely studied for its potential adsorption capabilities for soluble N and P, but the performance of different types of biochars can vary widely. In this review, we summarized the adsorption capacities of biochars in removing N (NH_4-N and NO_3-N) and P (PO_4-P) based on the reported data, and discussed the possible mechanisms and influencing factors. In general, the NH_4-N adsorption capacity of unmodified biochars is relatively low, at levels of less than 20 mg/g. This adsorption is mainly via ion exchange and/or interactions with oxygen-containing functional groups on biochar surfaces. The affinity is even lower for NO_3-N, because of electrostatic repulsion by negatively charged biochar surfaces. Precipitation of PO_4-P by metals/metal oxides in biochar is the primary mechanism for PO_4-P removal. Biochars modified by metals have a significantly higher capacity to remove NH_4-N, NO_3-N, and PO_4-P than unmodified biochar, due to the change in surface charge and the increase in metal oxides on the biochar surface. Ambient conditions in the aqueous phase, including temperature, pH, and co-existing ions, can significantly alter the adsorption of N and P by biochars, indicating the importance of optimal processing parameters for N and P removal. However, the release of endogenous N and P from biochar to water can impede its performance, and the presence of competing ions in water poses practical challenges for the use of biochar for nutrient removal. This review demonstrates that progress is needed to improve the performance of biochars and overcome challenges before the widespread field application of biochar for N and P removal is realized.

Contents

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1. Nutrients in water

Nitrogen (N) and phosphorus (P) are essential elements required in the structure and functions of living organisms, such as N in protein synthesis formation and P in genetic material, cell membranes, and energy transfer (Marschner and Marschner 2012). However, excessive inputs of anthropogenic nutrients into aquatic systems have led to the eutrophication in rivers, lakes, reservoirs, and estuaries worldwide, subsequently leading to algal blooms that threaten drinking water safety and the biodiversity of aqueous ecosystems (Conley et al. 2009, Woodward et al. 2012, Xia et al. 2020). In the aqueous phase, inorganic N and P, which are the main drivers of eutrophication, mainly exist in the form of ammonium (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}) (Yin et al., 2018a).

It is the simultaneous presence of N and P (NH_4^+ and PO_4^{3-}, NO_3^- and PO_4^{3-}) that causes algal blooms, while the presence of N alone (NH_4^+ and NO_3^-) does not lead to blooms (Zeng et al. 2016). Studies conducted as early as the 1970s suggest that P is the primary limiting nutrient (Schindler 1974). Reducing P loading has been shown to inhibit eutrophication in lakes, though it was unable to improve water quality in other water bodies such as estuaries and marine waters (Conley et al. 2009). Therefore, a dual-nutrient-reduction strategy for controlling both P and N in water is necessary for eutrophication control. (Conley et al. 2009).

Massive amounts of N- and P-rich products are produced and used for industrial, agricultural, and domestic purposes. Excess N and P may be released into aqueous environments via industrial effluents, agricultural runoff, and municipal wastewater systems (Fig. 1). Although wastewater treatment plants (WWTPs) remove the majority of N and P to lower their concentration below local standard guidelines before final discharge into natural waterways and bodies, they are still recognized as one of the main sources of N and P in receiving natural waters. In addition to the anthropogenic sources, atmospheric precipitation, biological nitrogen fixation, and the decomposition of organic matter in sediments may also contribute to the total N and P loading in aquatic ecosystems.

Many processes have been developed to remove nutrients from wastewater. The modified Ludzak-Ettinger (MLE) process is a common process for biological nitrogen removal (Song et al. 2015), in which ammonia in wastewater is converted into nitrate and subsequently gaseous nitrogen by nitrification and denitrification, respectively. Processes based on anaerobic ammonium oxidation (anammox) to convert ammonia with nitrite to nitrogen gas have

been developed and applied (Zhang et al. 2008). High ammonia concentration in wastewater inhibits the activities of microorganisms involved in nitrogen transformation, which has led to the coupled adoption of physicochemical methods, such as folding point chlorination, magnesium ammonium phosphate (MAP) precipitation and the airstrip process (Zhang et al. 2011). The biological process may also be adopted to remove phosphorus in wastewater, involving phosphate-accumulating organisms (PAOs) in the aerobic/oxic (A/O) process (Oehmen et al. 2007). PAOs have the ability to store and release phosphate in response to cyclical environmental conditions (Nielsen et al. 2019). Moreover, because phosphate can be precipitated by a variety of metals and metaloxides, chemical precipitation processes may be an alternative or supplementary method to biological processes (Ye et al. 2017). The sources and controls of anthropogenic N and P in the water environment are illustrated in Fig. 1.

Adsorption is an effective and rapid process for removing contaminants from the aqueous phase, depending on adsorbent properties and ambient electrolyte conditions. Many adsorbents have been evaluated for their effectiveness in the removal of N and P from water systems, including zeolites, bentonite, polymeric ion exchangers, nanoparticles, and aluminum oxides (Alshameri et al. 2018, Angar et al. 2017, Jorgensen and Weatherley 2003, Li et al. 2017, Niu et al. 2012, Xu et al. 2018, Zhang and Gao 2013).

Biochar is a carbon(C)-rich solid product formed through thermal decomposition of biomass, including agricultural and forestry waste, municipal sludge, manure, and other C-rich materials (Ahmad et al. 2014). The easy availability of feedstock and potentially low cost of production of biochar has made it a material of interest for environmental remediation in recent decades (Ahmad et al. 2014). The features of biochar that make it feasible for sorption include, but are not limited to, the high specific surface area, well-developed pore structure, high C content, abundant oxygen-containing functional groups, and high cation exchange capacity (Ahmad et al. 2014). The physical and chemical properties and the sorption selectivity and capacity of biochars has been shown to be related to both the feedstock and temperature of production (Hassan et al. 2020, Mukome et al. 2013). Furthermore, metallic elements in biochar may also play an indispensable role in adsorption (Wang et al., 2020b, Yin et al., 2018a). Biochar applied in soil may bind nutrients like NH_4^+, NO_3^- and PO_4^{3-} through specific and non-specific adsorption (Hale et al. 2013), and therefore serve as a N- or P-enriched input (Spokas et al. 2012). Thus,
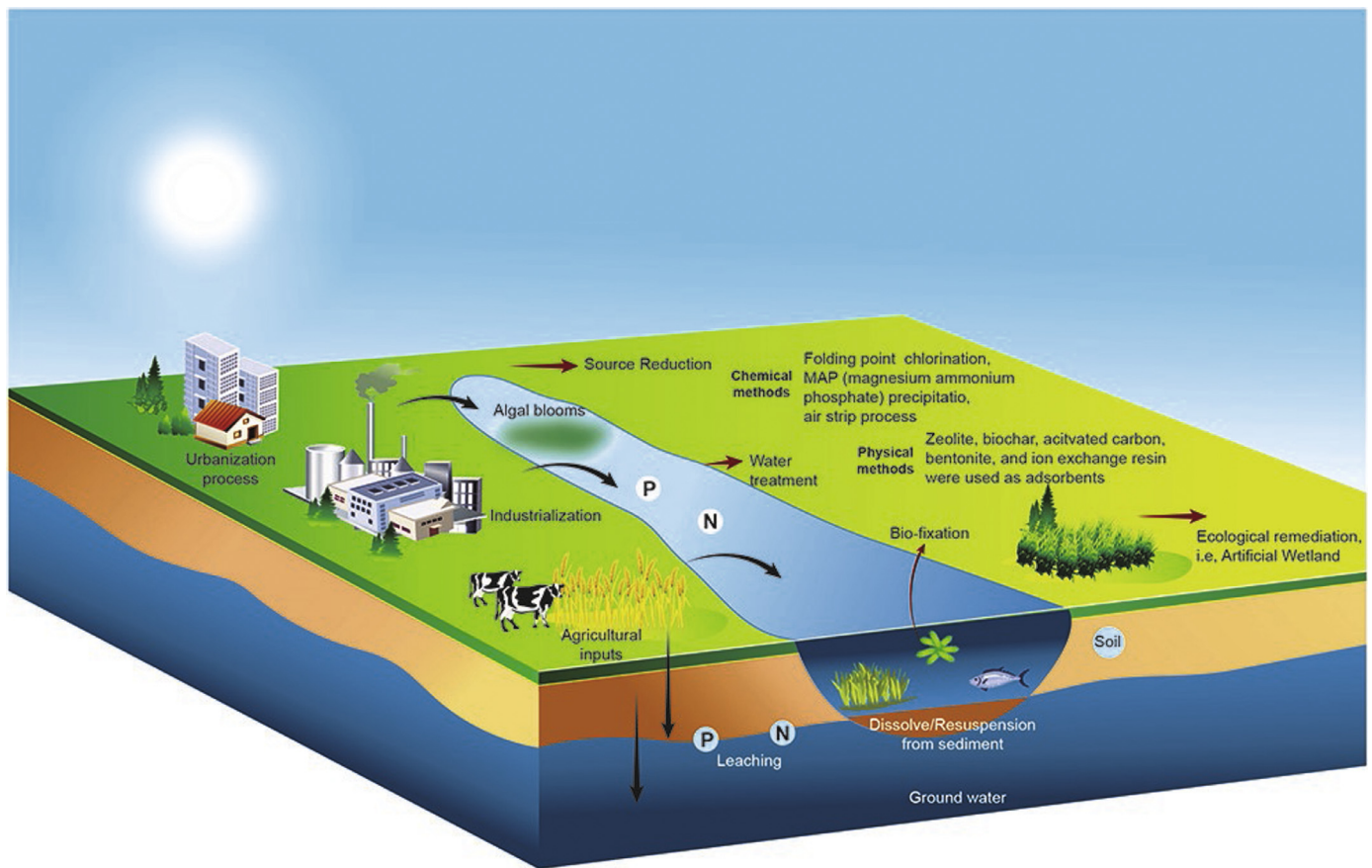
Fig. 1. Source and control of nutrients (N and P) in the water environment.

undesirable contaminants in aqueous environments can be transformed into desirable nutrients in the cropping system. Nutrient leaching in soil may also be mitigated through these processes. Additionally, biochar has been shown to sequester ammonia in a stable form for at least 12 days, during which it may be available for plant uptake (Taghizadeh-Toosi et al. 2012).

Numerous studies have used biochar as an adsorbent for individually or simultaneously removing N (NH_4^+, NO_3^-) and P (PO_4^{3-}) from water (Afkhami et al. 2007, Chintala et al. 2013, Gai et al. 2014, Gao et al. 2015, Hale et al. 2013, Mizuta et al. 2004, Yang et al. 2017, Zeng et al. 2013). Reports reveal that nutrient removal efficiencies of biochars in water vary significantly as a function of the types and properties of biochars and the ambient conditions of the aqueous phase (Xiao and Pignatello 2016, Yao et al. 2013, Zhang et al. 2012). We search reported references in the database of Web of Science using the terms of "adsorption or sorption" and "biochar or charcoal" and "ammonium or nitrate or phosphate" as keywords. There are several review papers focused on the use of biochar for the removal of contaminants, including heavy metals, anionic contaminants, and organic contaminants, from water (Ahmed et al. 2016, Rajapaksha et al. 2016, Wang et al. 2019). However, to the best of our knowledge, no systematic review has been conducted on the capabilities and mechanisms of biochar and modified biochar for N and P removal in water. Based on the data from the literature, especially the maximum adsorption capacity (Q_{max}) as estimated by the Langmuir isotherm model, this review evaluates the performance and capacity of biochars for N and P removal, and explores the corresponding mechanisms and critical factors that may affect adsorption. For the purposes of comparison within this review, Q_{max} data from individual references has been converted into mg N/g or mg P/g. The

aim is to guide the development and application of biochar-based technology to remove various forms of N and P in aquatic environments of water systems.

2. Efficiencies of biochar for nutrient removal from water

2.1. Ammonium removal by biochar

2.1.1. Ammonium removal by unmodified biochar

Ammonium is one of the main inorganic forms of N in the aqueous phase, and the interconversion between ammonium and ammonia is pH and temperature-dependent (Emerson et al. 1975). Based on the calculation by Emerson et al. (1975), ammonium (NH_4^+) is the predominant form (>90%) over ammonia (NH_3) in most of the water environment with pH < 8.2 and temperature < 28°C. Extensive batch adsorption studies have been carried out to evaluate the removal efficiency of ammonium nitrogen (NH_4-N) by biochars of diverse feedstocks and production temperatures. For example, the potential application in NH_4-N adsorption has been evaluated for pine sawdust biochar, wheat straw biochar (Yang et al. 2017), peanut shell biochar, corncob biochar, cotton stalk biochar (Gao et al. 2015, Liu et al. 2016), and giant reed biochar (Hou et al. 2016). Q_{max} values of biochars for NH_4-N vary widely throughout the literature with a mean value of 11.19 mg N/g. The Q_{max} values for NH_4-N were 5.38 and 3.37 mg N/g in pine sawdust biochar pyrolyzed at 300 °C and 550 °C, respectively (Yang et al. 2017), and 1.21~1.49 mg N/g in giant reed biochar pyrolyzed at 500 °C (Hou et al. 2016). Much higher Q_{max} values for NH_4-N were observed for sesame straw biochars pyrolyzed at 300~700°C (14.81–26.84 mg/g) (Yin et al., 2018b). Cui et al. (2016) pyrolyzed biomass from 22 species of
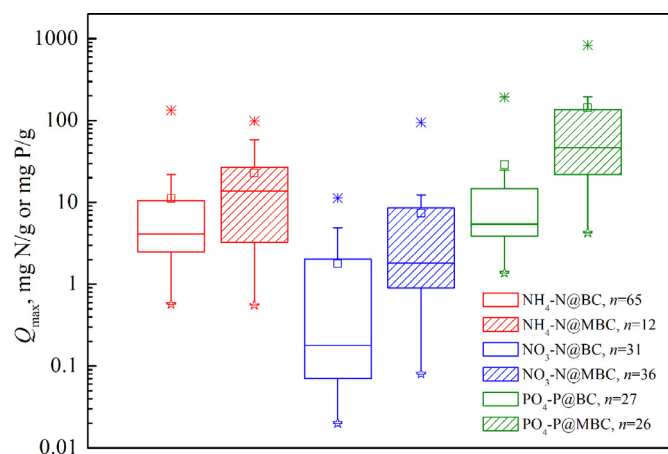
Fig. 2. Adsorption capacities (Q_{max}) of NH$_4$-N, NO$_3$-N, PO$_4$-P by biochar (BC) and modified biochar (MBC). The "∗" and "☆" are the maximum and minimum values, respectively. The upper and lower edge of the box is 75% and 25% of the data, and the cross line in the box is the median value and the "□" is the mean value. Bars over and below the box are the outlier limit, indicating that Q_{max} over this range is extremely better than the majority. Data were collected from cited literature, and n in the legend is the number of collected Q_{max} data (Detailed data and references are in Table S1).

plants obtained from constructed wetlands at 500 °C, and carried out a single-concentration (100 mg/L NH$_4$-N) adsorption test. The *Canna indica* biochar performed the best with a Q_{max} value of 7.71 mg N/g. In general, most reported NH$_4$-N adsorption capacities of biochar were below 20 mg N/g. However, a few exceptions with NH$_4$-N adsorption capacities up to 133 mg N/g have been observed (Fan et al. 2019, Kizito et al. 2015), which are summarized in Fig. 2. Detailed NH$_4$-N Q_{max} vales of different biochars are listed in Table S1 as supplementary material.

2.1.2. Ammonium removal by modified biochar

In order to improve the adsorption capacities of biochars for ammonium, attempts to increase CEC, enhance chemical precipitation, or alter biochar surface functional groups have been undertaken. For example, the addition of materials with high CEC into biochar feedstocks may significantly enhance the Q_{max} of ammonium, such as montmorillonite (Chen et al. 2017) and bentonite (Ismadji et al. 2015). Similarly, the adsorption isotherms for NH$_4^+$ by Mg-modified *Phragmites australis* biochar were almost linear, indicating unsaturated adsorption capacities with increasing NH$_4$-N concentrations, and a Q_{max} value of 32 mg N/g within the tested concentration range (Gong et al. 2017). Authors attribute this to the cationic exchange between Mg^{2+} and NH$_4^+$, as NH$_4^+$ adsorption was positively correlated with the release of Mg^{2+} (Gong et al. 2017). It has been suggested by Fan et al. (2019) that adsorption of NH$_4^+$ by phosphate-rich biochar was significantly enhanced in the presence Mg^{2+} through the precipitation of struvite (MgNH$_4$PO$_4$). While these studies provide new insight into modification strategies for enhancing biochar ammonium removal efficiency. Other modification methods, such as mild oxidation of biochar by H$_2$O$_2$ (Wang et al., 2015a), were not shown to significantly improve the adsorption capacity. Fig. 2 illustrates that the average and medium Q_{max} values of modified biochar for ammonium (22.79 mg N/g and 13.85 mg N/g, repsectively) are significantly higher than that of unmodified biochar (11.19 mg N/g and 4.12 mg N/g, repsectively), indicating modification may be an effective strategy to enhance the ammonium removal efficiency of biochars (Chandra et al. 2020).

2.2. Nitrate removal by biochar

In the aquatic phase, nitrate is present in the anionic form (NO$_3^-$) due to the full dissociation of HNO$_3$ in water. In theory, the electrostatic repulsion between nitrate and the negatively charged biochar surface constitutes one of the most significant barriers for nitrate adsorption on biochar. In this section, studies are reviewed to evaluate the effectiveness of biochars as adsorbents for nitrate removal during wastewater treatment or remediation in natural waters.

2.2.1. Nitrate removal by unmodified biochar

Although biochars derived from a broad range of biomass feedstocks and pyrolysis conditions have been tested for their nitrate adsorption capacity (Fig. 2), few biochars have been shown to effectively interact with nitrate. These observations are in accordance with the theoretical assumption.

The majority of studies demonstrate that unmodified biochar had almost no, or minimal, adsorption capacity for nitrate. For example, no nitrate removal in aqueous solution was observed for 12 biochars derived from 3 feedstocks in batch adsorption tests, among which some biochars even released rather than adsorbed nitrate (Gai et al. 2014). Similar results were also observed for biochars derived from corn stover and oak wood pyrolyzed at 300-450 °C (Hollister et al. 2013), cacao shell and corn cob pyrolyzed at 300-350 °C (Hale et al. 2013), and sugarcane bagasse, peanut hull, pepperwood, and bamboo pyrolyzed at 300-450 °C (Yao et al. 2012). These negligible nitrate removal efficiencies are most likely due to the electrostatic repulsion between the negatively charged biochar surface and the nitrate anion.

Limited nitrate adsorption by biochars has been observed in some studies. Kameyama et al. (2012) evaluated the performance of sugarcane bagasse-derived biochar and found that the adsorption isotherm best fit the Freundlich adsorption model, though adsorption was weak with values less than 0.8 mg N/g at equilibrium concentrations above 100 mg N/L. Yao et al. (2012) found that biochars derived from sugarcane bagasse, peanut hull, pepperwood, and bamboo can slightly adsorb nitrate when the pyrolysis temperature increased to 600 °C. Similar values (1.25 mg N/g) were also achieved by bamboo powder biochar produced at 900 °C (Mizuta et al. 2004), 3.27 mg N/g by corncob biochar pyrolyzed at 600 °C (Zhao et al. 2018), and 2.02 mg N/g by oak sawdust pyrolyzed at 600 °C (Wang et al., 2015b), corn stover (8.68 mg N/g), ponderosa pinewood residue (2.58 mg N/g), and switchgrass (8.75 mg N/g) pyrolyzed at 650 °C using the microwave (Chintala et al. 2013). Higher pyrolysis temperature (>600 °C) may explain the adsorption capacity of these biochars, as it can lead to altered physicochemical, such as higher surface area and lower O-containing functional groups (Ahmad et al. 2014). Increased surface area may also increase the number of biochar sorption sites, while decreased O-containing functional groups may reduce the electrostatic repulsion between biochar and nitrate. However, it should be noted that even where biochar nitrate sorption was observed, values were fairly low, with average Q_{max} value of 1.78 mg N/g (Fig. 2, Table S1), indicating that unmodified biochar may not be an effective strategy for nitrate removal for aqueous environments.

2.2.2. Nitrate removal by modified biochar

Substantial modification of biochars may facilitate their nitrate adsorption capacity, especially where modifications hinder the electrostatic repulsion between nitrate ions and biochar. Common modification strategies include protonation of negatively charged functional groups and metal/metal oxide impregnation into biochar or biochar feedstocks. For example, treating biochar with concentrated HCl has been shown to effectively increase nitrate adsorption capacity of biochars (Chintala et al. 2013). In that study, the

highest level of enhancement for nitrate adsorption was found in HCl-modified Ponderosa pinewood residue biochar, which adsorbed 9.74 mg N/g, compared to 2.58 mg N/g in the unmodified biochar. Authors hypothesize this enhanced adsorption to be the result of a significant increase in surface area (~10x) following HCl modification (Chintala et al. 2013). Biochar pyrolyzed from Lanthanum (La)-immersed sawdust was also found to significantly enhance the nitrate adsorption capacity of oak sawdust biochar from 2.02 mg N/g (unmodified) to 22.58 mg N/g. The authors hypothesized that an increase of basic functional groups in La modified biochar is responsible for the enhancement of nitrate removal (Wang et al., 2015b). In another study, MgO-modified biochar nanocomposite by immersing biomass feedstocks into $MgCl_2$ solution before pyrolysis elevated nitrate adsorption capacities as high as 95 mg N/g (Zhang et al. 2012). High-resolution transmission electron microscopy revealed the morphology of MgO-modified biochar was altered with increased spaces of 2 to 4 nm between the MgO nano-flakes, which may have served as new adsorption sites for anions (Zhang et al. 2012). The average Q_{max} of modified biochar for nitrate is 7.42 mg N/g (Table S1), which is about 3.8x of unmodified biochar.

2.3. Phosphate removal by biochar

2.3.1. Removal of phosphate by unmodified biochar

The inorganic form of P (PO_4-P) in water presents in different anionic forms, such as $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, depending on environmental pH. Consistent with the observations for NO_3^-, phosphate anions are usually repelled by the negatively charged surfaces of biochar. As a result, the adsorption capacities of unmodified biochars for inorganic P are generally low. Cui et al. (2016) compared twenty-two biochars derived from wetland plants for their sorption capability of PO_4-P, and found that only 4 biochars exhibited positive PO_4-P removal from the aqueous phase, indicating weak interactions between biochar and PO_4-P. In addition, the desorption of PO_4-P from biochars was observed rather than adsorption. Gong et al. (2017) found that the biochar derived from *Phragmites australis* (600 °C) had little impact on the total phosphorus (TP) levels in samples from a eutrophic lake and its inflow river. The ability of biochar to adsorb PO_4-P also appears biomass dependent. For example, biochar derived from peanut shells (700 °C) had much greater capacity for PO_4-P removal (2.0 mg P/g at 20 °C) than biochars pyrolyzed at 700 °C derived from oak wood, soybean, and bamboo wood, and the later two biomass derived biochar even released rather than adsorbed P (Jung et al. 2015). The significant lower Mg/P and Ca/P ratios in these two biochars were hypothesized to be responsible for the P desorption, as divalent cation bridging may be the primary binding mechanism for phosphorus on biochar (Jung et al. 2015). Higher PO_4-P removal efficiencies have been observed by corn biochar pyrolyzed at 300, 450, and 600 °C(with Q_{max} values up to 190 mg P/g) (Fig. 2), though no specific explanation was provided regarding this unusually high Q_{max} (Fang et al. 2014). The Q_{max} of biochar for phosphate ranges from 1.37 to 193 mg P/g, with average value of 28.90 mg P/g (Table S1).

2.3.2. Phosphate removal by modified biochar

As with nitrate removal, researchers have attempted to increase phosphate adsorption by adding metals and metal oxides to biochar feedstocks with mixed results (Ajmal et al. 2020, Chandra et al. 2020, Wang et al., 2020a, Zeng et al. 2013) (Fig. 2). Mg is the most widely studied, as it can significantly promote the PO_4-P adsorption capacity of biochar due to the stong divalent cation bridging between Mg and P (Jung et al. 2015, Wang et al., 2020b). Intrinsic Mg present in the tissues of biochar

feedstocks has also been shown to promote P sorption. For instance, Zeng et al. (2013) found that biochar derived from a phytoremediation plant, *Thalia dealbata*, has a higher PO_4-P adsorption capacity (about 2.54~4.96 mg P/g) compared to three other phytoremediation plants with negligible P removal efficiencies. Authors hypothesize this to be the result of the higher Mg content in *Thalia dealbata* than other plants was believed to be the main reason. Yao et al. (2013) found biochar derived from Mg-enriched tomato leaves capable of adsorbing high amounts of PO_4-P (>100 mg PO_4-P/g). They also concluded that the P-loaded biochar might potentially be used as a soil amendment or a slow-release fertilizer, as it contains more than 10% P. These findings led to an interest in modifying biochar by adding Mg to enhance its PO_4-P adsorption capacity. While some investigations resulted in no significant increase of PO_4-P adsorption in Mg-modified biochar (Fang et al. 2014), others found an extraordinary increase from almost 0 to nearly 109 mg PO_4-P/g (Gong et al. 2017). The highest level of PO_4-P retention (835 mg P/g) was from a MgO-modified biochar pyrolyzed from $MgCl_2$ immerged sugar beet tailing at 600 °C (Zhang et al. 2012). Differences in the effect of Mg-modification on PO_4-P adsorption capacity may be attributed to many factors, including differences in intrinsic biochar properties, the concentration of added Mg, and pyrolysis conditions.

Additional metals such as La and Al have also been reported to be effective in enhancing biochar PO_4-P removal. The PO_4-P adsorption capacity of oak sawdust biochar (500 °C) was enhanced from 10.44 mg P/g by the untreated to 46.57 mg P/g by La modified biochars (Wang et al., 2015b). Novais et al. (2018) found that biochar derived from poultry manure and sugarcane straw (350 °C) can adsorb significant amounts of Al. Those Al-doped biochars then had extremely high Q_{max} values of 701.65 mg P/g and 758.96 mg P/g, respectively. The Al-doping process can effectively cover the negatively charged biochar surface while forming positive adsorption sites for PO_4-P, functioning as "Al-bridges" between biochar and PO_4-P and facilitating the adsorption/precipitation of P (Novais et al. 2018). Further evaluation is necessary for the application of Al-doped biochar in water treatment, as Al solubility and toxicity should also be considered in aqueous environments and particularly in natural water bodies. It can be clearly shown in Fig. 2 and Table S1 that biochar modification can significantly enhance the removal of phosphate. The average Q_{max} of modified biochar for phosphate is 143.10 mg P/g, which is about 4.95x of unmodified biochar.

In a recent study, Wang et al. (2020b) increased the anion exchange capacity via treating biochars (hardwood and softwood at 500 °C) with a cationic polymer [poly(diallyldimethylammonium) chloride; pDADMAC] leading to an substantial increase of PO_4-P sorption, approximately 1000 times greater than unmodified biochars. The authors compared this result with MgO doped biochars and found that the pDADMAC was comparable in sorption capacity, but that sorption reversibility was greater for the pDADMAC modified biochars.

3. Mechanisms of nutrient removal by biochar

In order to further understand the removal of N and P by unmodified biochar and modified biochars, factors governing the adsorption process, such as surface area, ion exchange, surface functional group interaction, and precipitation, are illustrated in Fig. 3.

3.1. Surface area

The specific surface area (SA) is generally considered a critical parameter governing the adsorption capacity of carbonaceous materials. Because SA is directly related to the density of adsorption sites per unit of mass, the increase of SA is
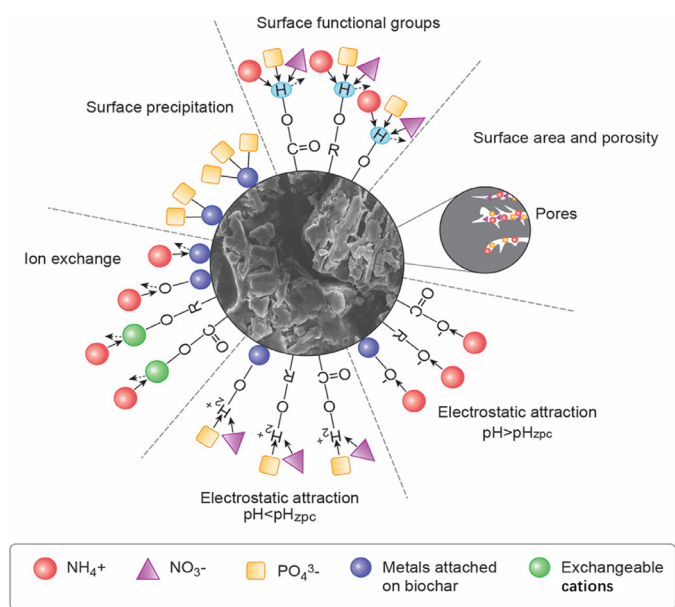
Fig. 3. Suggested mechanisms for the adsorption of NH_4-N, NO_3-N, and PO_4-P.

expected to lead to higher adsorption capacity. This is supported multiple times throughout the literature. For example, Zeng et al. (2013) found that with the increase of pyrolysis temperature (500-700 °C), the SA of biochars significantly increased, which elevated the adsorption capacities for ammonium and phosphate; Chintala et al. (2013) found that concentrated HCl treated biochars have a nearly 10x higher SA, which significantly improved their adsorption capacities for nitrate. By contrast, Yang et al. (2017) evaluated NH_4^+ adsorption by three biochars with SAs of 189.2, 55.24, and <1 m^2/g, and found their adsorption capacities to be negatively correlated with SA. Similarly, Takaya et al. (2016) found that biochars with higher SA did not necessarily adsorb more NH_4^+. These cases suggest that SA is not the sole determinant of NH_4^+ adsorption. It is worth noting that the increase of SA correlates with the loss of oxygen-containing functional groups, which may also play an important role in NH_4^+ adsorption. Details concerning surface functional groups will be further discussed in section 3.3.

While increasing SA may improve NH_4^+ adsorption, the same may not be true for the adsorption of anions (e.g., NO_3^-, PO_4^{3-}) as the surface of biochar is most commonly negatively charged (Wang et al., 2015b, Yao et al. 2013, Zeng et al. 2013).

3.2. Ion exchange

Negatively charged biochar surfaces balance with positively charged cations in aqueous environments. It has been observed that low-temperature biochars may have a higher CEC, and therefore lead to higher NH_4^+ adsorption capacity (Yang et al. 2017). This may suggest that NH_4^+ is adsorbed by replacing other cations with lower affinities for the surface sites of biochar. A similar conclusion was reached by Gai et al. (2014), who found that biochar pyrolyzed at lower temperatures (400 °C and 500 °C) had higher CEC than those pyrolyzed at higher temperatures (600 °C and 700 °C). In this study, the highest NH_4^+ removal was observed in the biochar with the highest CEC. In addition to pyrolysis temperature, biochar CEC is closely related to the properties of its feedstocks. For example, corn straw-derived biochars had significantly higher CEC and NH_4^+ removal efficiency than those derived from peanut shell or wheat straw at all pyrolysis temperatures (Gai et al. 2014). Modification with the addition of metals may

enhance biochar CEC, thus increase the adsorption for NH_4^+. One study by Gong et al. (2017) illustrated this by demonstrating that NH_4^+ sorption by Mg-modified *Phragmites australis* biochar is predominantly governed by ion exchange between NH_4^+ and Mg^{2+}.

3.3. Surface functional groups

The surface chemistry of biochar is largely characterized by hydrophobicity at higher pyrolysis temperatures and negatively charged surface functional groups at lower temperatures, many of which typically contain oxygen (e.g., -OH, COOH). As a result, biochars can have some affinity for NH_4^+. However, the lack of surface functional groups that carry a net positive charge minimizes electrostatic attraction of NO_3^- and PO_4^{3-} to biochars. The adsorption of ammonia on oxidized carbon surface of graphite oxides generally involves reactions with oxygen-containing functional groups to form amines and amides, as NH_4^+ acts as a Brønsted or Lewis acid (Seredych and Bandosz 2007). Thus, it is reasonable to expect that the abundance of oxygen-containing functional groups, including carboxyl, on biochar surfaces, may be closely related to NH_4^+ adsorption. For example, low-temperature-derived biochars with higher O/C mole ratios can have much higher NH_4^+ adsorption capacity, as chemical bonding or electrostatic interactions are formed between O-containing functional groups on biochar surfaces and NH_4^+ (Yang et al. 2017).

Interactions between NH_4-N and O-containing functional groups can be elucidated by examining property changes before and after NH_4^+ adsorption. To our knowledge, no direct evidence from biochar samples is currently available, while the adsorption of NH_4^+ by biomass (strawberry powder) has been examined: following NH_4^+ loading, Liu et al. (2010) observed a new peak in the FT-IR spectrum of strawberry powder at 1549 cm^{-1}, which is recognized as the overlap band of the N-H bending vibration and C-N stretching. Some peak shifts in the spectrum of samples before and after NH_4^+ adsorption were attributed to the binding of NH_4^+ to hydroxyl, phenolic, and carboxyl groups (Liu et al. 2010).

The protonation and deprotonation of surface functional groups is impacted by solution pH and can significantly influence bonding between O-containing functional groups and NH_4^+, therefore influence the resultant adsorption of NH_4^+ by biochars. The removal efficiency of NH_4^+ by wood and rice husk biochar (600 °C) was much lower at lower pH (Kizito et al. 2015), which can be attributed to the protonation of functional groups (C=O, COO$^-$) on the biochar surface, which results in weakened ionic bond formation between NH_4^+ and biochar. As biochar surfaces are primarily negatively charged, anions such as PO_4^{3-} and NO_3^- are typically repelled rather than adsorbed. The effect of pH is further discussed in section 4.3.

3.4. Precipitation

The formation of magnesium and calcium phosphates on biochar surfaces is considered the primary mechanism of PO_4^{3-} removal from water (Cui et al. 2016, Yao et al. 2013). The high ratios of magnesium and calcium to phosphorus (Mg/P=3.46 and Ca/P=47.6, respectively) of a peanut shell biochar (700 °C), for example, were used to explain its high PO_4^{3-} adsorption capacity (Jung et al. 2015). A positive correlation between the Ca and Mg contents of biochars and phosphate adsorption was also observed by Takaya et al. (2016). Authors found that only a small fraction of P-loading was reversible through desorption, suggesting the formation of a stable P composite on the biochar surface. Scanning electronic microscopy and X-ray photoelectron spectroscopy images have revealed nano-scale Mg-P precipitates closely adhered to biochar surfaces (Yao et al. 2013).

4. Factors influencing nutrient removal by biochar

4.1. Pyrolysis conditions

Unmodified biochars typically have very low capacity for NO_3^- and PO_4^{3-} irrespective of pyrolysis conditions. However, it is well established that biochars pyrolyzed at lower temperatures retain more anionic functional groups and thus exhibit higher adsorption capacity for NH_4^+ than those pyrolyzed at higher temperatures (as discussed in subsection 3.3). For example, Yang et al. (2017) observed Q_{max} values of pine sawdust biochar pyrolyzed at 300 °C and 550 °C to be 5.38 and 3.37 mg N/g, respectively. Similarly, Gai et al. (2014) studied twelve biochars from three types of biomass pyrolyzed at four temperatures, to report that the sorption of NH_4^+ was negatively dependent with pyrolysis temperature.

The negative relationship between NH_4^+ Q_{max} and pyrolysis temperature is attributed to the loss of N-, H-, and O-containing polar functional groups at higher temperatures (Keiluweit et al. 2010). Relatedly, the significant decrease in CEC with the increase of pyrolysis temperature has been considered the main contributor to the decrease in Q_{max}, since ion exchange is believed to be the predominant mechanism in the process of NH_4^+ adsorption (Gai et al. 2014, Yang et al. 2017). Furthermore, the increased temperature may increase the aromaticity and hydrophobicity of biochar surfaces (Ahmad et al. 2014, Mukome et al. 2013), thereby weakening contact of biochar with the hydrophilic NH_4^+.

Increasing biochar production temperature has often been linked to decreasing ammonium adsorption, inconsistencies exist in the literature. Yao et al. (2012) reported no significant relationship between the adsorption of NH_4^+ and pyrolysis temperature, while Zeng et al. (2013) observed an increase in adsorption capacity towards both NH_4^+ and PO_4^{3-} at higher temperatures. The significant increase of surface area with the increase of pyrolysis temperature (500 to 700 °C) was believed to be the main reason. Although Li et al. (2018) observed a decrease of ammonium adsorption by biosolid biochar with the increase of pyrolysis temperature, inconsistencies were found in this study regarding the adsorption of ammonium by switchgrass biochar and water oak biochar. These contrary findings indicate that multiple mechanisms govern the adsorption of N and P.

4.2. Co-existing ions

As described above, cation exchange is a dominant mechanism for the removal of NH_4^+ from aqueous solution. As a result, the presence of competing cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} may decrease NH_4^+ adsorption to biochar (Yang et al. 2017). This may be especially relevant for cations with higher bonding affinities towards biochar than NH_4^+. Divalent cations are typically stronger competitors as they have greater charge density and can occupy more adsorption sites on biochar (Yang et al. 2017). While Hou et al. (2016) demonstrated that increasing cation concentration decreased the NH_4^+ adsorption capacity of giant reed biochar, authors also reported that divalent cations (Ca^{2+} and Mg^{2+}) competed more weakly with NH_4^+ than the monovalent cations (Na^+ and K^+). The intensity of competition between NH_4^+ and other cations depends on their relative electric affinity for the given functional groups, and pH-related variable charge at biochar surfaces.

Anion adsorption by biochars is governed by the intensity and affinity of positively charged sites generated by metals and metal oxides at biochar surfaces, except for specific complexation via covalent bonds. Novais et al. (2018) observed that the affinity of anions to biochar increased with the increasing surface charge of biochar and decreasing hydrated ionic radius, indicating an electrostatic interaction between biochar and anions. Anions such as phosphate and sulfate may compete with nitrate for adsorption on biochars (Chintala et al. 2013). It is expected that the more negatively charged anions would occupy more available adsorption sites on the biochar surface, leading to a significant decrease in nitrate adsorption to biochar. The net nitrate adsorption by biochars would depend on the relative affinities of nitrate to adsorption sites compared to other anions. Yao et al. (2013) observed that anions such as Cl^-, NO_3^-, HCO_3^- compete with PO_4^{3-}, thereby decreasing P adsorption. This effect was strongest when these three competing ions were mixed in solution together. The reduction of P adsorption by each anion separately was less than 20%, while P adsorption was reduced by nearly 40% when anions were mixed. Authors hypothesized that anions like Cl^- and NO_3^- could not precipitate with Mg in the engineered biochar, and the reduction of P adsorption was caused by the completion or blocking of the surface adsorption sites. Competition among Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-} for adsorption sites was also observed on Al-doped biochar (Novais et al. 2018). Fang et al. (2014) similarly found that P adsorption by biochar decreased slightly in swine wastewater compared to artificial wastewater, likely due to the presence of competing anions in swine wastewater.

4.3. Ambient pH

Aqueous pH not only influences the chemical form of ions but also alters the variable charge on biochar surfaces via protonation and deprotonation of surface functional groups, thus affecting ion adsorption processes. Yang et al. (2017) reported that NH_4^+ adsorption by three biochars was significantly increased with increasing pH. Similar trends were observed for the sorption of NH_4^+ from swine manure anaerobically digested slurry by wood and rice husk biochars (Kizito et al. 2015). At lower pH, the H^+ ions may strongly compete against NH_4^+ for the adsorption sites on the biochar surface, thus inhibiting NH_4^+ adsorption and removal efficiency. Moreover, the protonation of negatively charged functional groups on the biochar surface hinders the interaction between NH_4^+ and biochar (Kizito et al. 2015, Yang et al. 2017). Chintala et al. (2013) found that increasing pH weakened the adsorption of nitrate on biochars, mainly due to the dissociation and deprotonation of functional groups on the biochar surface, which lead to electrostatic repulsion between nitrate and biochar surfaces.

It was similarly observed that increasing pH had a negative effect on the removal of anionic phosphate due to the pH-dependent speciation of P ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) in the aqueous phase (Fang et al. 2014). As pH increases, the form of P tends to have increased negative charge density. This, combined with the deprotonation of biochar surface functional groups, results in increased electrostatic repulsion and decreased P adsorption. Furthermore, OH^- ions at higher pH may also compete with P for sorption sites on the biochar surface. Li et al. (2016) reported that layered double hydroxides (LDH)-modified biochar performed best for P removal at low pH (e.g. pH = 3). The authors demonstrated that the protonation of biochar surface functional groups at low pH under zero-point charge (pH_{zpc}) resulted in an increase in positive surface charge, which is believed to enhance the adsorption of phosphate (Li et al. 2016).

4.4. Ambient temperature

Adsorption processes are influenced by the ambient temperature of aqueous environments due to both physical diffusion and heat exchange processes (i.e., endothermic/exothermic reactions). Increasing the ambient temperature from 25 to 40 to 50 °C resulted in a decrease in the NH_4^+ adsorption capacity of cotton

stock biochar and NaOH-modified cotton stock biochar pyrolyzed at 300 °C (Gao et al. 2015, Liu et al. 2016), as the adsorption of NH_4^+ was shown to be an exothermic process. However, the opposite result was reported by Kizito et al. (2015), who found that the adsorption of NH_4^+ from swine manure anaerobic digested slurry by wood and rice husk biochars increased as the temperature increased from 15 to 45 °C, implying an endothermic process. One explanation is that higher temperatures may facilitate the diffusivity of adsorbed NH_4^+ into the inner structure of biochar, thus leading to the elevated adsorption.

The sorption of nitrate by biochar has also been shown to be temperature-dependent. The nitrate adsorption capacity of biochar derived from bamboo biochar decreased (from 1.25 mg N/g to about 1.0 mg N/g) as the temperature increased (from 10 to 20 °C) (Mizuta et al. 2004), which suggests that the adsorption of nitrate by bamboo biochar is an exothermic process. Increasing the temperature from 25 to 45 °C enhanced the adsorption of PO_4^{3-} by corn biochar, and the thermodynamic calculation suggested that the sorption is an endothermic and spontaneous process (Fang et al. 2014). This result was corroborated by Jung et al. (2015), who found that the increase of ambient temperature from 10 to 30 °C promoted the adsorption of PO_4^{3-} by peanut shell biochar. In this study, the rising Langmuir constant with increased temperature indicates that the adsorption affinity increases at higher temperatures. It has been speculated that increasing temperature can promote the random thermal motion of ions, which may enhance the likelihood of collision between phosphate and adsorption sites on biochar (Kilic et al. 2013, Wang et al. 2016).

5. Challenges and perspectives

Biochars may contain considerable amounts of endogenous N and P depending on the composition of their biomass feedstocks. As such, biochar may become the source of nutrients in water through the release of inorganic N and P. Yao et al. (2012) studied the leaching of NH_4^+ and NO_3^- from biochars, and found that among tested thirteen biochars, four of them released rather than removed NH_4^+, while nine of them released NO_3^-. Similarly, Chen et al. (2017) observed the slow release of NH_4^+ from biochar into the aqueous solution, accounting for 0.3%–4.92% of total NH_4^+. The release of NO_3^- in unmodified biochar was also observed by Gai et al. (2014). Cacao shell and corn cob biochars released 1483 mg/kg and 172 mg/kg PO_4-P, respectively, in a 60-day continuous leaching study (Hale et al. 2013). Park et al. (2015) reported even higher levels of phosphate release from sesame straw biochar, ranging from 62.6 mg/g to 168.2 mg/g as pyrolysis temperature increased. High levels of PO_4^{3-} released into the aqueous phase may be attributed to the low binding affinity of phosphate to biochar with low metal (Ca and Mg) contents (Jung et al. 2015). Significant phosphate release was observed by Cui et al. (2016), who reported that 17 of 22 tested biochars released PO_4^{3-} into the aqueous phase with a maximum amount of 3.68 mg P/g biochar. Latest research has shown that inherent or added alkali metals in biochar can dramatically alter the leaching of P from biochar, which has important implications for engineering of biochar for water treatment applications (Buss et al. 2020). At higher initial PO_4^{3-} concentration level, biochar tends to adsorb rather than release PO_4^{3-}. Therefore, the "net adsorption" of PO_4^{3-} in the biochar-aqueous system is determined by both the adsorption of exogenous PO_4^{3-} to biochar and the release of endogenous PO_4^{3-} from biochar into the water. The amount of xenobiotic PO_4^{3-} adsorbed by biochar increases as its initial concentration in aqueous phase increases, while the release of endogenous PO_4^{3-} is maintained at a constant level. Negative values occur when the concentration levels are rel-
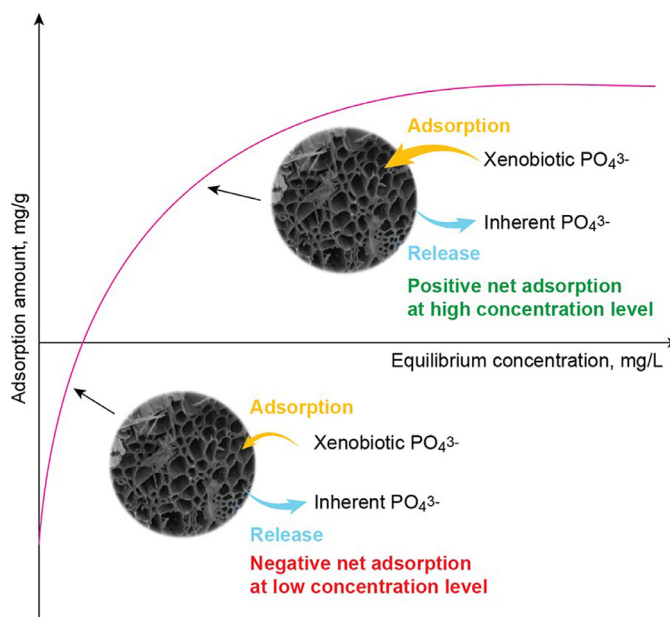

Fig. 4. Illustration of apparent net adsorption of phosphate by biochar.

atively low, while positive values occur at relatively high concentration levels (Fig. 4).

In addition, ions present in natural water bodies and/or wastewater environments act as strong competitors with NH_4^+, NO_3^-, and PO_4^{3-}, and consequently decrease their adsorption to biochar. Cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, can significantly compete with NH_4^+, while anions, such as Cl^-, HCO_3^-, SO_4^{2-}, negatively impact the removal of NO_3^- and/or PO_4^{3-}. It has been observed that more than 90% of the NH_4-N adsorbed to maple wood biochar can be desorbed in a KCl solution, indicating a significant replacement of NH_4^+ by K^+ (Wang et al., 2015a), it has been observed that a pure water solution can extract more than 20% of P adsorbed to poultry manure biochar and sugarcane straw biochar after 4 extraction rounds, while more than 90% was extracted with a solution of HCO_3^- (Novais et al. 2018). Therefore, the application of unmodified and modified biochar for the removal of nutrients from water is challenging, in terms of the high variability of expected effectiveness. Not only because the endogenous nutrients in biochar can be potential sources under certain circumstances (especially when N and P in water are present at low concentrations), but also of the competition posed by the other ions that are abundant in water/wastewater.

Though biochar and its modifications have been deeply investigated for their ability to remove P and N from water, uncertainty remains due to differences in biochar properties and those of the aqueous environment. Additionally, the sorption capacities of biochars in the current studies are largely determined by single-run batch adsorption experiments under controlled laboratory conditions, which are difficult to extrapolate to field conditions. The reusability, the stability, and the regeneration of biochar and modified biochar after use also need more investigations. As a result, careful evaluations should be given to choosing biochars for the removal of N and P from water and standardization of production and modification methods may be necessary before practical deployment of biochar for combating eutrophication. Furthermore, the potential contaminants in biochars (Gelardi et al. 2019), as well as the cost and potential secondary pollution of modifying biochars, should also be taken into consideration.

6. Conclusions

The removal of nitrogen (NH_4-N, NO_3-N) and phosphorus (PO_4-P) from water via adsorption by unmodified and modified biochar has been extensively studied, with data revealing variable efficacy. Removal efficiencies have been explained via ion exchange, biochar surface functional group interaction, or precipitation. However, the evidence so far has suggested that the majority of unmodified biochars only weakly adsorb N and P, which is especially true for the anionic forms of N and P due to electrostatic repulsion elicited by the negatively charged biochar surface. Modification is necessary to significantly enhance the adsorption capability of biochars for N and P removal by reducing the electrostatic repulsion or enhancing surface interactions, though the cost and environmental risks of biochar modification have yet to be fully explored. Therefore, challenges still exist for the development of cost-effective, environmentally friendly, field applicable biochar adsorbents for nutrient removal from water.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2020.116303.

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