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

1  **Evaluating biochar and its modifications for the removal of**

2  **ammonium, nitrate, and phosphate in water**

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**Abstract:** Removal of nitrogen (N) and phosphorus (P) from water and wastewater 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 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 and wastewater poses practical challenges for the use of biochar for nutrient removal. In conclusion, more 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.

**Keywords**: Biochar; Nutrient removal; Adsorption; Biochar modification; Water remediation

Contents

## 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 suggeste 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 (Figure 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,

108 atmospheric precipitation, biological nitrogen fixation, and the decomposition of organic

109 matter in sediments may also contribute to the total N and P loading in aquatic ecosystems.

110     Many processes have been developed to remove nutrients from wastewater. The

111 modified Ludzak-Ettinger (MLE) process is a common process for biological nitrogen

112 removal (Song et al. 2015), in which ammonia in wastewater is converted into nitrate and

113 subsequently gaseous nitrogen by nitrification and denitrification, respectively. Processes

114 based on anaerobic ammonium oxidation (anammox) to convert ammonia with nitrite to

115 nitrogen gas have been developed and applied (Zhang et al. 2008). High ammonia

116 concentration in wastewater inhibits the activities of microorganisms involved in nitrogen

117 transformation, which has led to the coupled adoption of physicochemical methods, such

118 as folding point chlorination, magnesium ammonium phosphate (MAP) precipitation and

119 the airstrip process (Zhang et al. 2011). The biological process may also be adopted to

120 remove phosphorus in wastewater, involving phosphate-accumulating organisms (PAOs)

121 in the aerobic/oxic (A/O) process (Oehmen et al. 2007). PAOs have the ability to store

122 and release phosphate in response to cyclical environmental conditions (Nielsen et al.

123 2019). Moreover, because phosphate can be precipitated by a variety of metals and metal-

124 oxides, chemical precipitation processes may be an alternative or supplementary method

125 to biological processes (Ye et al. 2017). The sources and controls of anthropogenic N and

126 P in the water environment are illustrated in **Figure 1**.

127

128 **<u>Figure 1</u>**

129

130     Adsorption is an effective and rapid process for removing contaminants from the

131 aqueous phase, depending on adsorbent properties and ambient electrolyte conditions.

132 Many adsorbents have been evaluated for their effectiveness in the removal of N and P

133  from water systems, including zeolites, bentonite, polymeric ion exchangers,

134  nanoparticles, and aluminum oxides (Alshameri et al. 2018, Angar et al. 2017, Jorgensen

135  and Weatherley 2003, Li et al. 2017, Niu et al. 2012, Xu et al. 2018, Zhang and Gao 2013).

136  Biochar is a carbon(C)-rich solid product formed through thermal decomposition

137  of biomass, including agricultural and forestry waste, municipal sludge, manure, and

138  other C-rich materials (Ahmad et al. 2014b). The easy availability of feedstock and

139  potentially low cost of production of biochar has made it a material of interest for

140  environmental remediation in recent decades (Ahmad et al. 2014b). The features of

141  biochar that make it feasible for sorption include, but are not limited to, the high specific

142  surface area, well-developed pore structure, high C content, abundant oxygen-containing

143  functional groups, and high cation exchange capacity (Ahmad et al. 2014b). Furthermore,

144  metallic elements in biochar may also play an indispensable role in adsorption (Yin et al.

145  2018a). Biochar applied in soil may bind nutrients like $NH_4^+$, $NO_3^-$ and $PO_4^{3-}$ through

146  specific and non-specific adsorption (Hale et al. 2013), and therefore serve as a N- or P-

147  enriched input (Spokas et al. 2012). Thus, undesirable contaminants in aqueous

148  environments can be transformed into desirable nutrients in cropping system. Nutrient

149  leaching in soil may also be mitigated through these processes. Additionally, biochar has

150  been shown to sequester ammonia in a stable form for at least 12 days, during which it

151  may be available for plant uptake (Taghizadeh-Toosi et al. 2012).

152  Numerous studies have used biochar as an adsorbent for individually or

153  simultaneously removing N ($NH_4^+$, $NO_3^-$) and P ($PO_4^{3-}$) from water/wastewater (Afkhami

154  et al. 2007, Chintala et al. 2013, Gai et al. 2014, Gao et al. 2015, Hale et al. 2013, Mizuta

155  et al. 2004, Yang et al. 2017, Zeng et al. 2013). Reports reveal that nutrient removal

156  efficiencies of biochars in water and wastewater vary significantly as a function of the

157  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. Based on the data from these literature, espeicially the maximum amount of adsorption ($Q_{max}$) estimated by Langmuir isotherm model, this review evaluates the performance and capacity of biochars for N and P removal, and the corresponding mechanisms and critical factors that may affect adsorption. All the $Q_{max}$ data from each individual reference is converted into mg N/g or mg P/g for the better comparability. 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 and wastewater systems.

## 2. Efficiencies of biochar for nutrient removal from water and wastewater

### 2.1 Ammonium removal by biochar

#### 2.1.1 Ammonium removal by unmodified biochar

Ammonium is one of the main inorganic form of N in aqueous phase, and the interconversion between ammonium and ammonia happens in the aqueous phase, which is pH and temperature dependant (Emerson et al. 1975). Based on the calculation by Emerson et al. (1975), ammonium ($NH_4^+$) is the predominant form (>90%) versus ammonia ($NH_3$) in most of the water environment with pH<8.2 and temperature<28℃. Extensive batch adsorption studies have been carried out to evaluate the removal efficiency of ammonium nitrogen ($NH_4$-N) by biochars of diverse feedstock and production temperature. 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

7

182  throughout the literatures with mean value of 11.19 mg N/g. The $Q_{max}$ values for NH4-N

183  were 5.38 and 3.37 mg N/g in pine sawdust biochar pyrolyzed at 300 °C and 550 °C,

184  respectively (Yang et al. 2017), and 1.21~1.49 mg N/g in giant reed biochar pyrolyzed at

185  500 °C (Hou et al. 2016). Much higher $Q_{max}$ values for NH4-N were observed with sesame

186  straw biochars pyrolyzed at 300~700°C (14.81–26.84 mg/g) (Yin et al. 2018b), which

187  presented more efficiently than most other biochars. Cui et al. (2016) pyrolyzed biomass

188  from 22 species of plants obtained from constructed wetlands at 500 °C, and carried out

189  a single-concentration (100 mg/L NH4-N) adsorption test. The *Canna indica* biochar

190  performed the best with a $Q_{max}$ value of 7.71 mg N/g. In general, most reported NH4-N

191  adsorption capacities of biochar were below 20 mg N/g. However, a few exceptions with

192  NH4-N adsorption capacities up to 133 mg N/g have been observed (Fan et al. 2019,

193  Kizito et al. 2015), which are summarized in Figure 2. Detailed NH4-N $Q_{max}$ vales of

194  different biochars are listed in Table S1 as supplementary material.

195  **Figure 2.**

196

197  *2.1.2 Ammonium removal by modified biochar*

198      In order to improve the adsorption capacities of biochars for ammonium, attempts

199  to increase CEC, enhance chemical precipitation, or alter biochar surface functional

200  groups have been undertaken. For example, the addition of materials with high CEC into

201  biochar feedstocks may significantly enhance the $Q_{max}$ of ammonium, such as

202  montmorillonite (Chen et al. 2017) and bentonite (Ismadji et al. 2015). Similarly, the

203  adsorption isotherms for $NH_4^+$ by Mg-modified *Phragmites australis* biochar were almost

204  linear, indicating unsaturated adsorption capacities with increasing NH4-N concentrations,

205  and its $Q_{max}$ was 32 mg N/g within the tested concentration range (Gong et al. 2017).

206  Authors attribute this to the cationic exchange between $Mg^{2+}$ and $NH_4^+$, as $NH_4^+$

207     adsorption was positively correlated with the release of $Mg^{2+}$ (Gong et al. 2017). It has

208     been suggested by Fan et al. (2019) that adsorption of $NH_4^+$ by phosphate-rich biochar

209     was significantly enhanced in the presence $Mg^{2+}$ through the precipitation of struvite

210     ($MgNH_4PO_4$). While these studies provide new insight into modification strategies for

211     enhancing biochar ammonium removal efficiency. Other modification methods, such as

212     mild oxidation of biochar by $H_2O_2$ (Wang et al. 2015a), were not shown to significantly

213     improve the adsorption capacity. Figure 2 illustrates that that the average and medium

214     $Q_{max}$ values of modified biochar for ammonium are significantly higher than that of

215     unmodified biochar, indicating modification may be an effective strategy to enhance the

216     ammonium removal efficiency of biochars.

217

218     ***2.2 Nitrate removal by biochar***

219     In the aquatic phase, nitrate is present in the anionic form ($NO_3^-$) due to the full

220     dissociation of $HNO_3$ in water. In theory, the electrostatic repulsion between nitrate and

221     the negatively charged biochar surface constitutes one of the most significant barriers for

222     nitrate adsorption on biochar. In this section, studies are reviewed to evaluate the

223     effectiveness of biochars as adsorbents for nitrate removal during wastewater treatment

224     or remediation in natural waters.

225     *2.2.1 Nitrate removal by unmodified biochar*

226     Although biochars derived from a broad range of biomass feedstocks and

227     pyrolysis conditions have been tested for their nitrate adsorption capacity (Figure 2), few

228     biochars have been shown to effectively interact with nitrate. These observations are is in

229     accordance with the theoretical assumption.

230     The majority of studies demonstrate that unmodified biochar had almost no, or

231     minimal, adsorption capacity for nitrate. For example, no nitrate removal in aqueous

232    solution was observed for 12 biochars derived from 3 feedstocks in batch adsorption tests,

233    among which some biochars even released rather than adsorbed nitrate (Gai et al. 2014).

234    Similar results were also observed for biochars derived from corn stover and oak wood

235    pyrolyzed at 300-450°C (Hollister et al. 2013), cacao shell and corn cob pyrolyzed at 300-

236    350°C (Hale et al. 2013), and sugarcane bagasse, peanut hull, pepperwood, and bamboo

237    pyrolyzed at 300-450°C (Yao et al. 2012). These negligible nitrate removal efficiencies

238    are most likely due to the electrostatic repulsion between the negatively charged biochar

239    surface and the nitrate anion.

240       Limited nitrate adsorption by biochars has been observed in some studies.

241    Kameyama et al. (2012) evaluated the performance of sugarcane bagasse-derived biochar

242    and found that the adsorption isotherm best fit the Freundlich adsorption model, though

243    adsorption was weak with values less than 0.8 mg N/g at equilibrium concentrations

244    above 100 mg N/L. Yao et al. (2012) found that biochars derived from sugarcane bagasse,

245    peanut hull, pepperwood, and bamboo can slightly adsorb nitrate when the pyrolysis

246    temperature increased to 600 °C. Smilar values (1.25 mg N/g) were also achieved by

247    bamboo powder biochar produced at 900 °C (Mizuta et al. 2004), 3.27 mg N/g by corncob

248    biochar pyrolyzed at 600°C (Zhao et al. 2018), and 2.02 mg N/g by oak sawdust pyrolyzed

249    at 600°C (Wang et al. 2015b), corn stover (8.68 mg N/g), ponderosa pinewood residue

250    (2.58 mg N/g), and switchgrass (8.75 mg N/g) pyrolyzed at 650°C using the microwave

251    (Chintala et al. 2013). Higher pyrolysis temperature (>600°C) may explain the adsorption

252    capacity of these biochars, as it can lead to altered physicochemical, such as higher

253    surface area and lower O-containing functional groups (Ahmad et al. 2014a). Increased

254    surface area may also increase the number of biochar sorption sites, while decreased O-

255    containing functional groups may reduce the electrostatic repulsion between biochar and

256    nitrate. However, it should be noted that even where biochar nitrate sorption was observed,

257  values were fairly low with average $Q_{max}$ value of 1.95 mg N/g (Figure 2, Table S1),

258  indicating that unmodified biochar may not be an effective strategy for nitrate removal

259  for aqueous environments.

260  *2.2.2 Nitrate removal by modified biochar*

261  Substantial modification of biochars may facilitate their nitrate adsorption capacity,

262  especially where modifcations hinder the electrostatic repulsion between nitrate ion and

263  biochar. Common modification strategies include protonation of negatively charge

264  functional groups, and metal/metal oxides impregnation into biochar or biochar

265  feedstocks. For example, treating biochar with concentrated HCl has been shown to

266  effectively increase nitrate adsorption capacity of biochars (Chintala et al. 2013). In that

267  study, the highest level of enhancement for nitrate adsorption was found in HCl-modified

268  Ponderosa pinewood residue biochar, which adsorbed 9.74 mg N/g, compared to 2.58 mg

269  N/g in the unmodified biochar. Authors hypothesize this enhanced adsorption to be the

270  result of a significant increase in surface area (~10x) following HCl modification

271  (Chintala et al. 2013). Biochar pyrolyzed from Lanthanum (La)-immersed sawdust was

272  also found to significantly enhance the nitrate adsorption capacity of oak sawdust biochar

273  from 2.02 mg N/g (unmodified) to 22.58 mg N/g. Authors hypothesized that the increase

274  of the basic functional groups in La modified biochar is responsible for the enhancement

275  of nitrate removal (Wang et al. 2015b). In another study, MgO-modified biochar

276  nanocomposite by immersing biomass feedstocks into $MgCl_2$ solution before pyrolysis

277  elevated nitrate adsorption capacities as high as 95 mg N/g (Zhang et al. 2012). High-

278  resolution transmission electron microscopy revealed the morphology of MgO-modified

279  biochar was altered with increased spaces of 2 to 4 nm between the MgO nano-flakes,

280  which may have served as new adsorption sites for anions (Zhang et al. 2012). The

281  average $Q_{max}$ of modified biochar for nitrate is 7.43 mg N/g (Table S1), which is about

11

### 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 aqueous phase, indicating a very weak interaction 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 believed to be responsible for the P desorption since divalent cation bridging is the main 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) (Figure 2), though no specific explanation was provided regarding this unusually high $Q_{max}$ (Fang et al. 2014). The $Q_{max}$ of biochar for phosphate

306 ranges from 1.4 to 193 mg P/g, with average value of 28.61 mg P/g(Table S1).

307 *2.3.2 Phosphate removal by modified biochar*

308 As with nitrate removal, researchers have attempted to increase phosphate adsorption by

309 adding metals and metal oxides to biochar feedstocks with mixed results (**Figure 2**). Mg

310 is the most widely studied, as it can significantly promote the $PO_4$-P adsorption capacity

311 of biochar due to the stong divalent cation bridging between Mg and P (Jung et al. 2015).

312 Intrinsic Mg present in the tissues of biochar feedstocks has also been shown to promote

313 P sorption. For instance, Zeng et al. (2013) found that biochar derived from a

314 phytoremediation plant, *Thalia dealbata*, has a higher $PO_4$-P adsorption capacity (about

315 2.54~4.96 mg P/g) compared to three other phytoremediation plants with negligible P

316 removal efficiencies. Authors hypothesize this to be the result of the higher Mg content

317 in *Thalia dealbata* than other plants was believed to be the main reason. Yao et al. (2013)

318 found biochar derived from Mg-enriched tomato leaves capable of adsorbing high

319 amounts of $PO_4$-P (>100 mg $PO_4$-P/g). They also concluded that the P-loaded biochar

320 may potentially be used as a soil amendment or a slow-release fertilizer, as it contains

321 more than 10% P. These findings led to an interest in modifiing biochar by adding Mg to

322 enhance its $PO_4$-P adsorption capacity. While some investigations resulted in no

323 significant increase of $PO_4$-P adsorption in Mg-modified biochar (Fang et al. 2014),

324 others found an extraordinary increase from almost 0 to nearly 109 mg $PO_4$-P/g (Gong et

325 al. 2017). The highest level of $PO_4$-P retention (835 mg P/g) was from a MgO-modified

326 biochar pyrolized from $MgCl_2$ immerged sugar beet tailing at 600°C (Zhang et al. 2012).

327 Differences in the effect of Mg-modification on $PO_4$-P adsorption capacity may be

328 attributed to many factors, including differences in intrinsic biochar properties, the

329 concentration of added Mg, and pyrolysis conditions.

330    Additional metals such as La and Al have also been reported to be effective in

331    enhancing biochar $PO_4$-P removal. The $PO_4$-P adsorption capacity of oak sawdust biochar

332    (500°C) was enhanced from 10.67 mg P/g by the untreated to 47.57 mg P/g by La

333    modified biochars (Wang et al. 2015b). Novais et al. (2018) found that biochar derived

334    from poultry manure and sugarcane straw (350°C) can adsorb significant amounts of Al.

335    Those Al-doped biochars then had extremely high $Q_{max}$ values of 701.65 mg P/g and

336    758.96 mg P/g, respectively. The Al-doping process can effectively cover the negatively

337    charged biochar surface while forming positive adsorption sites for $PO_4$-P, functioning as

338    "Al-bridges" between biochar and $PO_4$-P and facilitating the adsorption/precipitation of

339    P (Novais et al. 2018). Further evaluation is necessary for the application of Al-doped

340    biochar in wastewater treatment, as Al solubility and toxicity should also be considered

341    in aqueous environments and particularly in natural water bodies. It can be clearly shown

342    in Figure 2 and Table S1 that biochar modification can significantly enhance the removal

343    of phosphate. The average $Q_{max}$ of modified biochar for phosphate is 146.74 mg P/g,

344    which is about 5.13x of unmodified biochar.

345

346    **3. Mechanisms of nutrient removal by biochar**

347    In order to further understand the removal of N and P by unmodified biochar and modified

348    biochars, factors governing the adsorption process, such as surface area, ion exchange,

349    surface functional group interaction, and precipitation, are illustrated in Figure 3.

350

351    **Figure 3**

352

353    *3.1 Surface area*

354    The specific surface area (SA) is generally considered a critical parameter governing the

14

355     adsorption capacity of carbonaceous materials. Because SA is directly related to the

356     density of adsorption sites per unit of mass, the increase of SA is expected to lead to

357     higher adsorption capacity. This iss supported multiple times throughout the literature.

358     Zeng et al. (2013) found that with the increase of pyrolysis temperature (500-700 °C), the

359     SA of biochars significantly increased, which elevated the adsorption capacities for

360     ammonium and phosphate; Chintala et al. (2013) found that concentrated HCl treated

361     biochars have a nearly 10x higher SA, which significantly improved their adsorption

362     capacities for nitrate. By contrast, Yang et al. (2017) evaluated $NH_4^+$ adsorption by three

363     biochars with SAs of 189.2, 55.24, and <1 $m^2$/g, and found their adsorption capacities to

364     be negatively correlated with SA. Similarly, Takaya et al. (2016) found that biochars with

365     higher SA did not necessarily adsorb more $NH_4^+$. These cases suggest that SA is not the

366     sole determinant of $NH_4^+$ adsorption. It is worth noting that the increase of SA correlates

367     with the loss of oxygen-containing functional groups, which may also play an important

368     role in $NH_4^+$ adsorption. Details concerning surface functional groups will be further

369     discussed in section 3.3.

370     While increasing SA may improve $NH_4^+$ adsorption, the same may not be true for the

371     adsorption of $NO_3^-$, $PO_4^{3-}$ anions as the surface of biochar is most commonly negatively

372     charged (Wang et al. 2015b, Yao et al. 2013, Zeng et al. 2013).

373

374     *3.2 Ion exchange*

375     Negatively charged biochar surfaces balance with positively charged cations in aqueous

376     environments. It has been observed that low-temperature biochars may have a higher

377     CEC, and therefore lead to higher $NH_4^+$ adsorption capacity (Yang et al. 2017). This may

378     suggest that $NH_4^+$ is adsorbed by replacing other cations with lower affinities for the

379     surface sites of biochar. A similar conclusion was reached by Gai et al. (2014), who found

380   that biochar pyrolyzed at lower temperatures (400 °C and 500 °C) had higher CEC than

381   those pyrolyzed at higher temperatures (600 °C and 700 °C). In this study, the highest

382   $NH_4^+$ removal was observed in the biochar with the highest CEC. In addition to pyrolysis

383   temperature, biochar CEC is closely related to the properties of its feedstocks. For

384   example, corn straw-derived biochars had significantly higher CEC and $NH_4^+$ removal

385   efficiency than those derived from peanut shell or wheat straw at all pyrolysis temperature

386   (Gai et al. 2014). Modification with the addition of metals may enhance biochar CEC,

387   thus increase the adsorption for $NH_4^+$. One study by Gong et al. (2017) illustrated this by

388   demonstrating that $NH_4^+$ sorption by Mg-modifed *Phragmites australis* biochar is

389   predominantly governed by ion exchange between $NH_4^+$ and $Mg^{2+}$.

390

391   *3.3 Surface functional groups*

392   The surface chemistry of biochar is largely characterized by hydrophobicity at higher

393   pyrolysis temperatures and negatively charged surface functional groups at lower

394   temperatures, many of which typically contain oxygen (e.g., -OH, COOH). As a result,

395   biochars can have some affinity for $NH_4^+$. However, the lack of surface functional groups

396   that carry a net positive charge minimizes electrostatic attraction of $NO_3^-$ and $PO_4^{3-}$ to

397   biochars. The adsorption of ammonia on oxidized carbon surface of graphite oxides

398   generally involves reactions with oxygen-containing functional groups to form amines

399   and amides, as $NH_4^+$ acts as a Brønsted or Lewis acid (Seredych and Bandosz 2007). Thus,

400   it is reasonable to expect that the abundance of oxygen-containing functional groups,

401   including carboxyl, on biochar surfaces may be closely related to $NH_4^+$ adsorption. For

402   example, low-temperature-derived biochars with higher O/C mole ratios can have much

403   higher $NH_4^+$ adsorption capacity, as chemical bonding or electrostatic interactions are

404   formed between O-containing functional groups on biochar surfaces and $NH_4^+$ (Yang et

16

405　al. 2017).

406　　　Interactions between $NH_4$-N and O-containing functional groups can be elucidated

407　by examining property changes before and after $NH_4^+$ adsorption. To our knowledge, no

408　direct evidence from biochar samples is currently available, while the adsorption of $NH_4^+$

409　by biomass (strawberry powder) has been examined: following $NH_4^+$ loading, Liu et al.

410　(2010) observed a new peak in the FT-IR spectrum of strawberry powder at 1549 $cm^{-1}$,

411　which is recognized as the overlap band of the N-H bending vibration and C-N stretching.

412　Some peak shifts in the spectrum of samples before and after $NH_4^+$ adsorption were

413　attributed to the binding of $NH_4^+$ to hydroxyl, phenolic, and carboxyl groups (Liu et al.

414　2010).

415　　　The protonation and deprotonation of surface functional groups is impacted by

416　solution pH and can significantly influence bonding between O-containing functional

417　groups and $NH_4^+$, therefore influence the resultant adsorption of $NH_4^+$ by biochars. The

418　removal efficiency of $NH_4^+$ by wood and rice husk biochar (600°C) was much lower at

419　lower pH (Kizito et al. 2015), which can be attributed to the protonation of functional

420　groups (C=O, $COO^-$) on the biochar surface, which results in weakened ionic bond

421　formation between $NH_4^+$ and biochar. As biochar surfaces are primarily negatively

422　charged, anions such as $PO_4^{3-}$ and $NO_3^-$ are typically repelled rather than adsorbed. The

423　effect of pH is further discussed in seciont 4.3.

424

425　***3.4 Precipitation***

426　The formation of magnesium and calcium phosphates on biochar surfaces is considered

427　the primary mechanism of $PO_4^{3-}$ removal from water (Cui et al. 2016, Yao et al. 2013).

428　The high ratios of magnesium and calcium to phosphorus (Mg/P=3.46 and Ca/P=47.6,

429　respectively) of a peanut shell biochar (700°C) , for example, were used to explain its

430  high $PO_4^{3-}$ adsorption capacity (Jung et al. 2015). A positive correlation between the Ca

431  and Mg contents of biochars and phosphate adsorption was also observed by Takaya et

432  al. (2016). Authors found that only a small fraction of P-loading was reversible through

433  desorption, suggesting the formation of a stable P composite on the biochar surface.

434  Scanning electronic microscopy and X-ray photoelectron spectroscopy images have

435  revealed nano-scale Mg-P precipitates closely adhered to biochar surfaces (Yao et al.

436  2013).

437

438  **4. Factors influencing nutrient removal by biochar**

439  *4.1 Pyrolysis conditions*

440  Unmodified biochars typically have very low capacity for $NO_3^-$ and $PO_4^{3-}$ irrespective of

441  pyrolysis conditions. However, it is well established that biochars pyrolyzed at lower

442  temperatures retain more anionic functional groups and thus exhibit higher adsorption

443  capacity for $NH_4^+$ than those pyrolyzed at higher temperatures (as discussed in subsection

444  3.3). For example, Yang et al. (2017) observed $Q_{max}$ values of pine sawdust biochar

445  pyrolyzed at 300 °C and 550 °C to be 4.66 and 1.27 mg N/g, respectively. Similarly, Gai

446  et al. (2014) studied twelve biochars from three types of biomass pyrolyzed at four

447  temperatures, to report that the sorption of $NH_4^+$ was negatively dependent with pyrolysis

448  temperature.

449      The negative relationship between $NH_4^+$ $Q_{max}$ and pyrolysis temperature is

450  attributed to the loss of N-, H-, and O-containing polar functional groups at higher

451  temperatures (Keiluweit et al. 2010). Relatedly, the significant decrease in CEC with the

452  increase of pyrolysis temperature has been considered the main contributor to the

453  decrease in $Q_{max}$, since ion exchange is believed to be the predominant mechanism in the

454  process of $NH_4^+$ adsorption (Gai et al. 2014, Yang et al. 2017). Furthermore, the increased

455 temperature may increase the aromaticity and hydrophobicity of biochar surfaces (Ahmad

456 et al. 2014a), thereby weakening contact of biochar with the hydrophilic $NH_4^+$.

457       Increasing biochar production temperature has often been linked to decreasing

458 ammonium adsorption, inconsistencies exist in the literature. Yao et al. (2012) reported

459 no significant relationship between the adsorption of $NH_4^+$ and pyrolysis temperature,

460 while Zeng et al. (2013) observed an increase in adsorption capacity towards both $NH_4^+$

461 and $PO_4^{3-}$ at higher temperatures. The significant increase of surface area with the

462 increase of pyrolysis temperature (500 to 700 °C) was believed to be the main reason.

463 Although Li et al. (2018) observed a decrease of ammonium adsorption by biosolid

464 biochar with the increase of pyrolysis temperature, inconsistencies were found in this

465 study regarding the adsorption of ammonium by switchgrass biochar and water oak

466 biochar. These contrary findings indicate that multiple mechanisms govern the adsorption

467 of N and P.

468

### 4.2 Co-existing ions

470 As described above, cation exchange is a dominant mechanism for the removal of $NH_4^+$

471 from aqueous solution. As a result, the presence of competing cations such as $Na^+$, $K^+$,

472 $Ca^{2+}$, and $Mg^{2+}$ may decrease $NH_4^+$ adsorption to biochar (Yang et al. 2017). This may

473 be especially relevant for cations with higher bonding affinities towards biochar than

474 $NH_4^+$. Divalent cations are typically stronger competitors as they have greater charge

475 density and can occupy more adsorption sites on biochar (Yang et al. 2017). While Hou

476 et al. (2016) demonstrated that increasing cation concentration decreased the $NH_4^+$

477 adsorption capacity of giant reed biochar, authors also reported that divalent cations ($Ca^{2+}$

478 and $Mg^{2+}$) competed more weakly with $NH_4^+$ than the monovalent cations ($Na^+$ and $K^+$).

479 The intensity of competition between $NH_4^+$ and other cations depends on their relative

480  electric affinity for the given functional groups, and pH-related variable charge at biochar

481  surfaces.

482  Anion adsorption by biochars is governed by the intensity and affinity of positively

483  charged sites generated by metals and metal oxides at biochar surfaces, except for specific

484  complexation via covalent bonds. Novais et al. (2018) observed that the affinity of anions

485  to biochar increased with the increasing surface charge of biochar and decreasing

486  hydrated ionic radius, indicating an electrostatic interaction between biochar and anions.

487  Anions such as phosphate and sulfate may compete with nitrate for adsorption on biochars

488  (Chintala et al. 2013). It is expected that the more negatively charged anions would

489  occupy more available adsorption sites on the biochar surface, leading to a significant

490  decrease in nitrate adsorption to biochar. The net nitrate adsorption by biochars would

491  depend on the relative affinities of nitrate to adsorption sites compared to other anions.

492  Yao et al. (2013) observed that anions such as $Cl^-$, $NO_3^-$, $HCO_3^-$ compete with $PO_4^{3-}$,

493  thereby decreasing P adsorption. This effect was strongest when these three competing

494  ions were mixed in solution together. The reduction of P adsorption by each anion

495  separately was less than 20%, while P adsorption was reduced by nearly 40% when anions

496  were mixtured. Authors hypothesized that, anions like $Cl^-$ and $NO_3^-$, could not precipitate

497  with Mg in the engineered biochar, and the reduction of P adsorption was caused by the

498  completion or blocking of the surface adsorption sites. Competition among $Cl^-$, $NO_3^-$,

499  $PO_4^{3-}$, $SO_4^{2-}$ for adsorption sites was also observed on Al-doped biochar (Novais et al.

500  2018). Fang et al. (2014) similarly found that P adsorption by biochar decreased slightly

501  in swine wastewater compared to artificial wastewater, likely due to the presence of

502  competing anions in swine wastewater.

503

504    *4.3 Ambient pH*

505    Aqueous pH not only influences the chemical form of ions but also alters the variable

506    charge on biochar surfaces via protonation and deprotonation of surface functional groups,

507    thus affecting ion adsorption processes. Yang et al. (2017) reported that $NH_4^+$ adsorption

508    by three biochars was significantly increased with increasing pH. Similar trends were

509    observed for the sorption of $NH_4^+$ from swine manure anaerobic digested slurry by wood

510    and rice husk biochars (Kizito et al. 2015). At lower pH, the $H^+$ ions may strongly

511    compete against $NH_4^+$ for the adsorption sites on the biochar surface, thus inhibiting $NH_4^+$

512    adsorption and removal efficiency. Moreover, the protonation of negatively charged

513    functional groups on the biochar surface hinders the interaction between $NH_4^+$ and

514    biochar (Kizito et al. 2015, Yang et al. 2017). Chintala et al. (2013) found that increasing

515    pH weakened the adsorption of nitrate on biochars, mainly due to the dissociation and

516    deprotonation of functional groups on the biochar surface which lead to electrostatic

517    repulsion between nitrate and biochar surfaces.

518    It was similarly observed that increasing pH had a negative effect on the removal of

519    anionic phosphate due to the pH-dependent speciation of P ($H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$)

520    in the aqueous phase (Fang et al. 2014). As pH increases, the form of P tends to have

521    increased negative charge density. This, combined with the deprotonation of biochar

522    surface functional groups, results in increased electrostatic repulsion and decreased P

523    adsorption. Furthermore, $OH^-$ ions at higher pH may also compete with P for sorption

524    sites on the biochar surface. Li et al. (2016) reported that layered double hydroxides

525    (LDH)-modified biochar performed best for P removal at low pH (e.g. pH = 3). The

526    authors demonstrated that the protonation of biochar surface functional groups at low pH

527    under zero-point charge ($pH_{zpc}$) resulted in an increase in positive surface charge, which

528    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.

22

554 2013, Wang et al. 2016).

555

556 **5. Challenges in using biochar for nutrient removal**

557 Biochars may contain considerable amounts of endogenous N and P depending on the

558 composition of their biomass feedstocks. As such, biochar may become the source of

559 nutrients in water through the release of inorganic N and P. Yao et al. (2012) studied the

560 leaching of $NH_4^+$ and $NO_3^-$ from biochars, and found that among tested thirteen biochars,

561 four of them released rather than removed $NH_4^+$, while nine of them released $NO_3^-$.

562 Similarly, Chen et al. (2017) observed the slow release of $NH_4^+$ from biochar into the

563 aqueous solution, accounting for 0.3%–4.92% of total $NH_4^+$. The release of $NO_3^-$ in

564 unmodified biochar was also observed by Gai et al. (2014). Cacao shell and corn cob

565 biochars released 1483 mg/kg and 172 mg/kg $PO_4^-$-P, respectively, in a 60-day continuous

566 leaching study (Hale et al. 2013). Park et al. (2015) reported even higher levels of

567 phosphate release from sesame straw biochar, ranging from 62.6 mg/g to 168.2 mg/g as

568 pyrolysis temperature increased. High levels of $PO_4^{3-}$ released into the aqueous phase

569 may be attributed to the low binding affinity of phosphate to biochar with low metal (Ca

570 and Mg) contents (Jung et al. 2015). Significant phosphate release was observed by Cui

571 et al. (2016), who reported that 17 of 22 tested biochars released $PO_4^{3-}$ into the aqueous

572 phase with a maximum amount of 3.68 mg P/g biochar. At higher initial $PO_4^{3-}$

573 concentration level, biochar tends to adsorb rather than release $PO_4^{3-}$. Therefore, the "net

574 adsorption" of $PO_4^{3-}$ in the biochar-aqueous system is determined by both the adsorption

575 of exogenous $PO_4^{3-}$ to biochar and the release of endogenous $PO_4^{3-}$ from biochar into the

576 water. The amount of xenobiotic $PO_4^{3-}$ adsorbed by biochar increases as its initial

577 concentration in aqueous phase increases, while the release of endogenous $PO_4^{3-}$ is

578 maintained at a constant level. Negative values occur when the concentration levels are

579  relatively low, while positive values occur at relatively high concentration levels (Figure

580  4).

581

582                                                    **Figure 4**

583

584  In addition, ions present in natural water bodies and/or wastewater environments act as

585  strong competitors with $NH_4^+$, $NO_3^-$, and $PO_4^{3-}$, and consequently decrease their

586  adsorption to biochar. Cations, such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, can significantly compete

587  with $NH_4^+$, while anions, such as of $Cl^-$, $HCO_3^-$, $SO_4^{2-}$, negatively impact the removal of

588  $NO_3^-$ and/or $PO_4^{3-}$. It has been observed that more than 90% of the $NH_4$-N adsorbed to

589  maple wood biochar can be desorbed in a KCl solution, indicating a significant

590  replacement of $NH_4^+$ by $K^+$ (Wang et al. 2015a). , it has been observed that a pure water

591  solution can extract more than 20% of P adsorbed to poultry manure biochar and

592  sugarcane straw biochar after 4 extraction rounds, while more than 90% was extracted

593  with a solution of $HCO_3^-$. (Novais et al. 2018).

594  Therefore, the application of biochar for the removal of nutrients from water is

595  challenging, in terms of the high variability of expected effectiveness. Not only because

596  the endogenous nutrients in biochar can be potential sources under certain circumstances

597  (especially when N and P in water are present at low concentrations), but also of the

598  competition posed by the other ions that are abundant in water/wastewater. As a result,

599  careful consideration should be made when choosing biochars for the removal of N and

600  P from water and wastewater systems in order to avoid inadvertently increasing the

601  release of these nutrients, and standardization of methods for the production and

602  modification of biochar may be necessary before practical deployment of biochar for

603  combating eutrophication. Furthermore, the potential contaminants in biochars, as well

604 as the cost and potential secondary pollution of modifying biochars, should also be taken

605 into consideration.

606

607 **6. Conclusions**

608 The removal of nitrogen (NH$_4$-N, NO$_3$-N) and phosphorus (PO$_4$-P) from

609 water/wastewater by biochar adsorption has been studied extensively, with data revealing

610 variable efficacy for biochar as an adsorbent. Removal efficiencies have been explained

611 via ion exchange and biochar surface functional group interaction or precipitation.

612 However, the evidence so far has suggested that the majority of unmodified biochars only

613 weakly adsorb N and P, which is especially true for the anionic forms of N and P due to

614 the electrostatic repulsion elicited by the negatively charged biochar surface.

615 Modification is necessary to significantly enhance the adsorption capability of biochars

616 for soluble and mineral forms of N and P species in water/wastewater, though the cost

617 and environmental risks of biochar modification have yet to be fully explored. Though

618 biochar and its modifications have been deeply investigated for their ability to remove P

619 and N from solution, uncertainty remains due to differences in biochar properties and

620 those of the aqueous environment. Differences between batch sorption studies such as

621 electrolyte composition and concentration or pH buffering strategies may also influence

622 the adsorption results. Furthermore, published studies so far have been mainly conducted

623 under controlled laboratory conditions, which are difficult to extrapolate to field

624 conditions. This is especially problematic considering the ions that naturally exist in water

625 and wastewater systems to compete with N and P, and the temperature and pH

626 fluctuations which may significantly alter the adsorption process. Therefore, biochars

627 should be evaluated under uniform conditions in order to reach conclusive findings and

628 provide guidance for practical applications in water/wastewater treatment in the future.

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841 **Figure 1.** Source and control of nutrients (N and P) in the water environment.
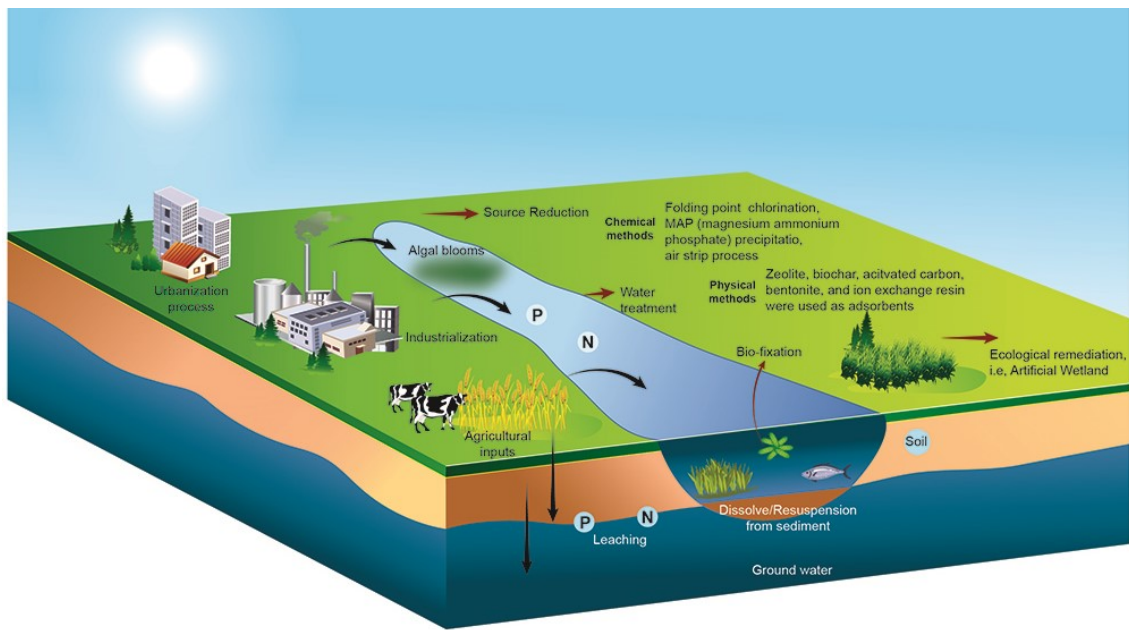


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844 **Figure 2**. Adsorption capacities ($Q_{max}$) of $NH_4$-N, $NO_3$-N, $PO_4$-P by biochar (BC) and modified

845 biochar (MBC). The "∗" and "☆" are the maximum and minimum values, respectively. The upper

846 and lower edge of the box is 75% and 25% of the data, and the cross line in the box is the median

847 value and the "□" is the mean value. Bars over and below the box are the outlier limit, indicating that

848 $Q_{max}$ over this range are extremely better than the majority. Data were collected from cited

849 literatures, and $n$ in the legend is the number of collected $Q_{max}$ data (Detailed data and references are

850 in Table S1).



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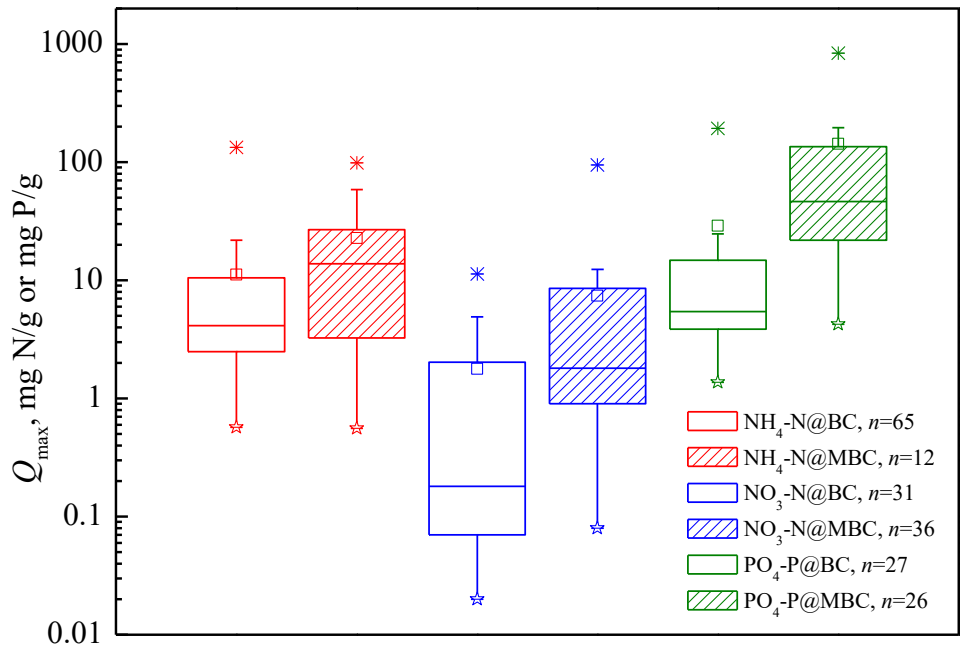
852 **Figure 3.** Suggested mechanisms for the adsorption of $NH_4$-N, $NO_3$-N, and $PO_4$-P.
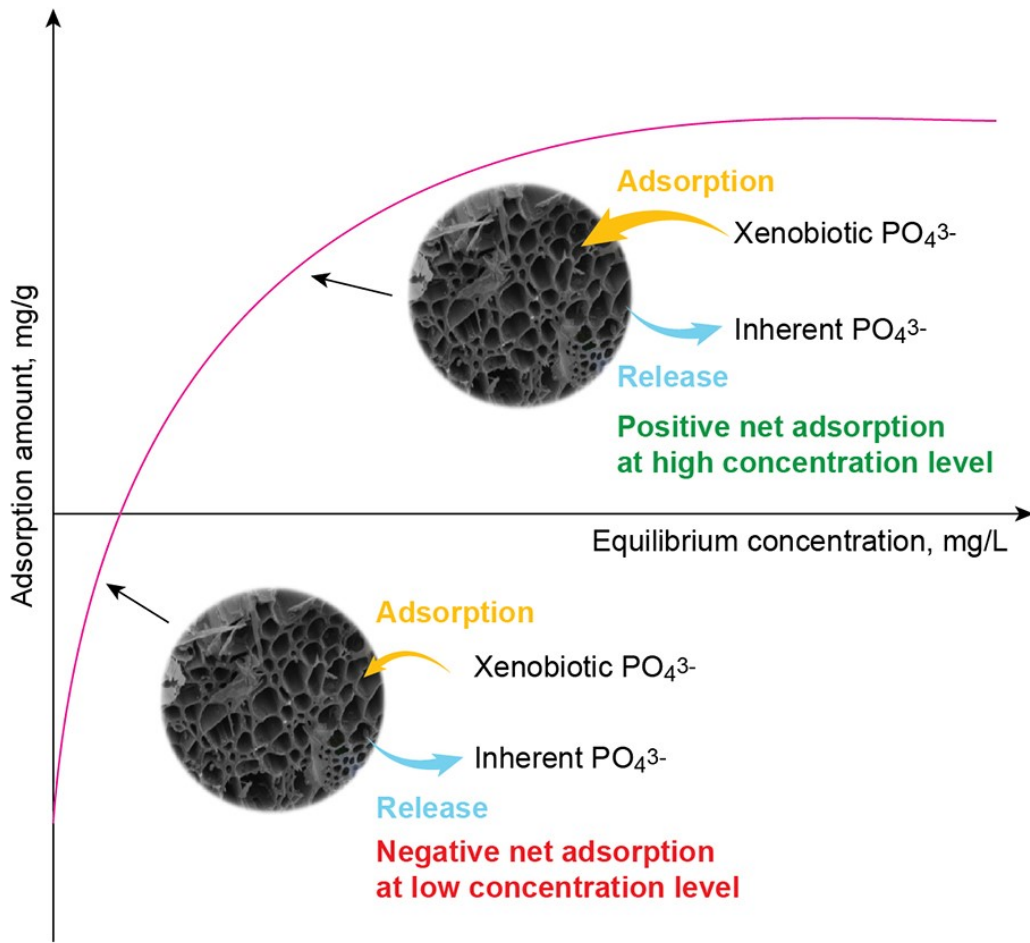
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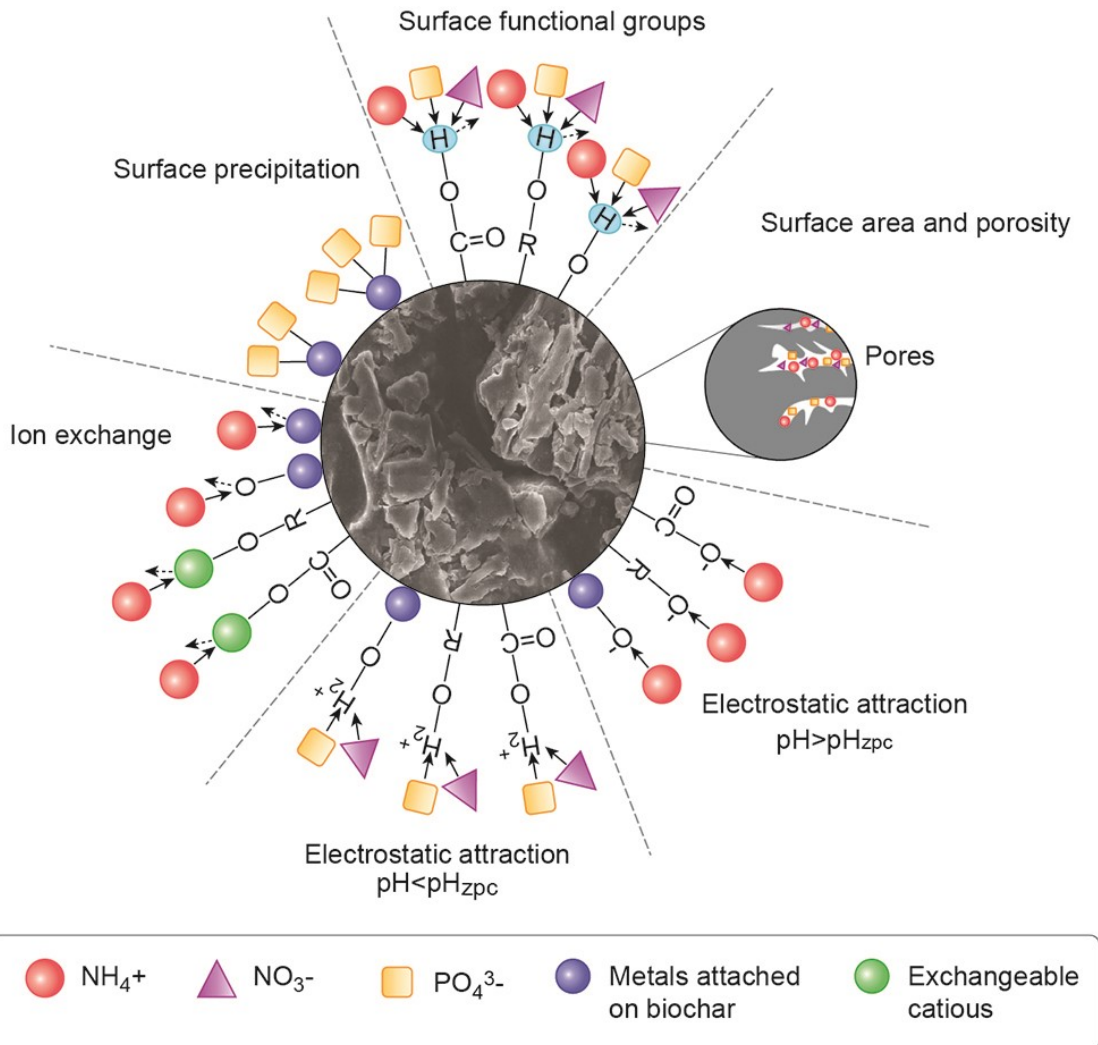


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856    **Figure 4**. Illustration of apparent net adsorption of phosphate by biochar.



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