

# NUTRIENTS' INTERACTIONS WITH BIOCHAR'S

## SURFACE CHEMISTRY

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### **Abstract**

Soil nutrients ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) are essential for crop growth. However, the presence of excess nutrients poses a significant environmental threat. Pyrogenic carbon materials, such as biochar, have gained attention in recent studies as fertilizer aids which can potentially mitigate nutrients from agricultural runoffs. Understanding interactions of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  with biochar's surface chemistry is critical in evaluating effectiveness of biochar in mitigating risks of nutrient leaching. Surface chemical properties of biochar such as surface functional groups, pH, and elemental and mineral composition have been found to influence  $\text{NO}_3^-$  and  $\text{NH}_4^+$  chemisorption mechanisms. The paper summarises the pertinent literature in this domain.

### **Introduction**

Retention of soil  $\text{NO}_3^-$  and  $\text{NH}_4^+$  can potentially reduce fertilizer application and decrease pollution associated with nutrient runoff and leaching. Biochar (BC) is found to reduce  $\text{NO}_3^-$  leaching from soil (Knowles et al., 2011) and also enhances localization of nitrate in rhizosphere improving plant nitrogen use efficiency (Prendergast-Miller et al., 2011). BC is known to retain  $\text{NH}_4^+$  as well (Nelson et al., 2011). Mukherjee et al. (2011) found that biochar's surface chemistry strongly influences chemisorption of adsorbates. Moreover, surface functional groups have been shown to play a critical role in chemisorption of nitrogen species (Padhye et al., 2010; Padhye et al., 2011; Huang et al., 2013). Elucidation of chemisorption mechanism for nutrients with BC is important to evaluate the potential of BC to mitigate nutrient runoff and leaching risks. The current review was carried out exclusively to understand the interaction of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  with BC surface chemistry.

### **Ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) interactions with biochar**

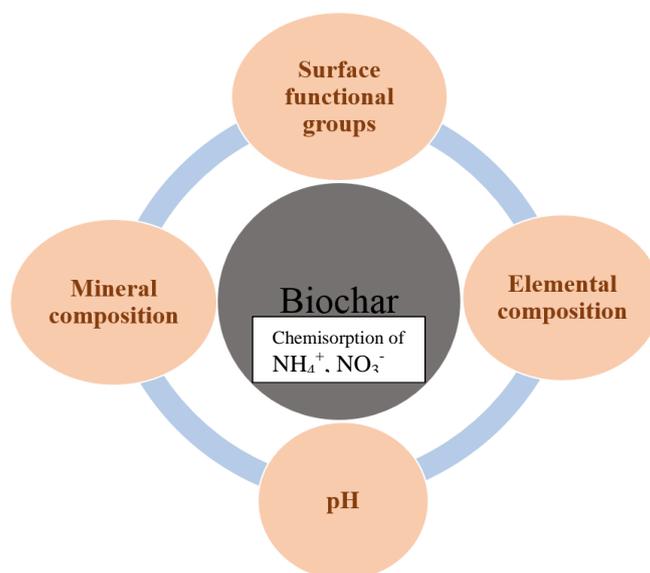
The most important factor which influences  $\text{NO}_3^-$  and  $\text{NH}_4^+$  adsorption is surface functional groups. Both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  interactions are strongly influenced by oxygen containing surface functional groups (OCSFGs). OCSFGs like carboxyl, phenols, lactones, etc. improve cation exchange capacity (CEC) of BC, which strongly attracts positively charged ions like  $\text{NH}_4^+$  (Angst et al., 2014; Esfandbod et al., 2017; Yin et al., 2007). OCSFGs are found to adsorb  $\text{NH}_4^+$  by forming hydrogen bonding between hydrogen of  $\text{NH}_4^+$  and oxygen from OCSFGs (Esfandbod et al., 2017).

Acidic functional groups create positive charge on the surface of BC which attracts negatively charged  $\text{NO}_3^-$  ion (Afkhami et al., 2007; Li et al., 2014). Basic functional groups, like pyridine and oxonium, increase anion exchange capacity, thereby improving  $\text{NO}_3^-$  adsorption (Lawrinenko and Laird, 2015; Lawrinenko et al., 2016) on the surface of BC.

O and H ratio on BC controls hydrophilic and hydrophobic properties (Ahmad et al., 2014; Fang et al., 2014). BC pyrolyzed at low temperature are hydrophilic in nature with high percent of OCSFGs, which is found to aid in water retention which indirectly increase  $\text{NO}_3^-$  retention by BC (Afkhami et al., 2007; Clough et al., 2013; Mangrich et al., 2015). High C:N ratio of BC induces  $\text{NH}_4^+$  and  $\text{NO}_3^-$  immobilization while low C:N results in mineralization (Robertson and Groffman, 2015).

BC which are basic in nature, containing high  $\pi$ -electrons, are suspected to donate electrons to water and during this process hydrogen bonding between water bound nutrients and electron rich BC is postulated (Kammann et al., 2015). If pH of matrix is higher than  $\text{pH}_{\text{zpc}}$  of BC, then  $\text{NH}_4^+$  ions adsorption occurs due to negative charge dominance on the surface of BC (Kizito et al., 2015). On the other hand low pH of matrix with higher  $\text{pH}_{\text{zpc}}$  of BC enhances attraction of negative ions like  $\text{NO}_3^-$  (Hafshejani et al., 2016).

Minerals present on BC, as well as elemental composition of BC, also alter nutrient interactions with the surface of BC. For example, oxidation of  $\text{Fe}_2^+$  to  $\text{Fe}_3^+$  on the surface of BC can result in reduction of  $\text{NO}_2^-$  to  $\text{NH}_4^+$  and  $\text{NO}_3^-$  to  $\text{NO}_2^-$  (Gao et al., 2016). Similarly, oxidation of  $\text{H}_2\text{S}$  and  $\text{S}^0$  to  $\text{SO}_4^{2-}$  can result in reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  (Burgin and Hamilton, 2007).



**Figure 1:** Four Principle Factors Affecting Chemisorption of Nutrients on Biochar

## Conclusions

From the literature, it is evident that the surface chemistry of biochar plays a prominent role in chemisorption of soil nutrients (Figure 1). OCSFGs are the most influential for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  adsorption. pH and elemental and mineral composition of BC also influence nutrient interactions to a great extent, which implies source of biochar and treatments given to it can be manipulated to produce BC with optimal surface chemistry for mitigating nutrient leaching risks. Elucidation of such fundamental chemisorption mechanisms is the need of the hour to predict fate of nutrients in soils amended with biochar.

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