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Chemical Principles Governing Biochar-Based Removal of Nutrients and Heavy Metals from Water

*Ilakkiya S, Manickavasagam S and Mahalakshmi S
Department of Aquatic Environment Management, TNJFU-Dr. M.G.R. Fisheries College & Research Institute, Ponneri, Thiruvallur, Tamil Nadu, India
*Corresponding Author's email: ilakkiyaS12@gmail.com

Biochar is a carbon-rich material produced through the thermochemical conversion of biomass under oxygen-limited conditions. Its porous structure, surface functional groups, mineral phases and variable surface charge enable the removal of nutrients and heavy metals from contaminated water. This article reviews the principal chemical mechanisms governing biochar performance, including ion exchange, electrostatic attraction, surface complexation, ligand exchange, precipitation and redox transformation. Particular attention is given to the removal of ammonium, nitrate, phosphate and representative heavy metals such as lead, cadmium, chromium, copper and zinc. The effects of pH, competing ions, feedstock, pyrolysis conditions and biochar modification are also discussed. Understanding these interactions is essential for designing effective, stable and environmentally sustainable biochar-based water-treatment systems.

Keywords: biochar; nutrient removal; heavy metals; adsorption mechanisms; water treatment

Introduction

Biochar is a carbon-rich material produced by the thermochemical conversion of biomass under oxygen-limited conditions. Its porous structure, surface functional groups, mineral constituents and surface charge make it useful for removing contaminants from water. Nutrients such as ammonium, nitrate and phosphate are major contributors to eutrophication, while heavy metals such as lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn) and chromium (Cr) are persistent and potentially toxic contaminants. Biochar can immobilize these pollutants through several chemical mechanisms, including ion exchange, electrostatic attraction, surface complexation, ligand exchange, precipitation and redox reactions (Ahmad et al., 2014; Li et al., 2017).

Chemical Properties of Biochar

Biochar contains aromatic carbon structures, pores and oxygen-containing functional groups such as carboxyl (-COOH), hydroxyl (-OH), phenolic and carbonyl groups. These groups undergo protonation and deprotonation according to water pH:

$$\text{–COOH} \rightleftharpoons \text{–COO}^- + H^+$$

The resulting negatively charged sites can attract positively charged ions such as NH_4^+ and metal ions. Biochar also contains mineral phases containing Ca, Mg, K, Fe and other elements that participate in ion exchange and precipitation reactions (Tan et al., 2015). Feedstock and pyrolysis temperature strongly influence these properties. High-temperature pyrolysis generally increases carbonization, aromaticity, porosity and mineral concentration, whereas lower-temperature biochars often retain more oxygen-containing functional groups. Therefore, biochars produced from different feedstocks can show substantially different contaminant-removal capacities (Ahmad et al., 2014; Thomas et al., 2020).

Nutrient Removal Mechanisms

Ammonium

Ammonium (NH_4^+) is primarily removed through cation exchange and electrostatic attraction. NH_4^+ can replace exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} associated with negatively charged biochar sites:

$$\textbf{Biochar–M} + NH_4^+ \rightarrow \textbf{Biochar–}NH_4 + M^+$$

The extent of removal depends on cation-exchange capacity, surface charge, pore structure and pH. However, pristine biochar may show limited ammonium adsorption, making surface modification useful for improving its performance (Yin et al., 2017; Zhang et al., 2020).

Nitrate

Nitrate (NO_3^-) is more difficult to remove because it is negatively charged. At neutral or alkaline pH, biochar surfaces are often negatively charged, resulting in electrostatic repulsion. Consequently, nitrate removal generally requires positively charged surfaces or modification with metal oxides and minerals that provide anion-binding sites (Zhang et al., 2020).

Phosphate

Phosphate is another negatively charged nutrient and is particularly important in eutrophication control. Its removal by pristine biochar may be limited, but Ca-, Mg-, Fe- and Al-containing biochars can provide effective reactive sites.

Phosphate can undergo **ligand exchange** with hydroxyl groups associated with metal oxides and form inner-sphere complexes. It can also precipitate with Ca and Mg:

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2(s)$$

Thus, phosphate removal is often controlled by chemical complexation and mineral precipitation rather than simple physical adsorption (Yin et al., 2017; Zhang et al., 2020).

Heavy Metal Removal Mechanisms

Biochar can remove heavy metals through several interacting mechanisms.

Electrostatic attraction and ion exchange

Negatively charged biochar surfaces attract cationic metals such as Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}. These metals can also replace exchangeable cations:

$$2\textbf{Biochar–Na} + Pb^{2+} \rightarrow (\textbf{Biochar})_2\textbf{–Pb} + 2Na^+$$

The importance of ion exchange depends on the biochar's cation-exchange capacity and mineral composition (Li et al., 2017).

Surface complexation

Heavy metals can form relatively strong chemical complexes with carboxyl, hydroxyl and phenolic groups:

$$2(–COO^-) + Pb^{2+} \rightarrow (–COO)_2Pb$$

Surface complexation generally provides stronger retention than simple electrostatic attraction and is an important mechanism for metals such as Pb and Cd (Li et al., 2017).

Precipitation

Biochar can increase solution alkalinity through the release of basic mineral components. Under suitable pH conditions, dissolved metals may precipitate as hydroxides, carbonates or phosphates. For example, Pb^{2+} can form poorly soluble lead carbonate or hydroxide phases. Precipitation can therefore contribute to long-term metal immobilization (Tan et al., 2015; Li et al., 2017).

Redox transformation

Some biochars contain redox-active groups and persistent radicals capable of changing the oxidation state of contaminants. Chromium is an important example. Reduction of Cr(VI) to Cr(III) can decrease chromium mobility and toxicity, after which Cr(III) may be retained through complexation or precipitation (Li et al., 2017).

Role of pH and Competing Ions

pH strongly controls biochar performance because it influences surface charge, functional-group ionization, contaminant speciation and mineral dissolution. Increasing pH commonly enhances the negative charge of biochar and favors the retention of cationic metals. However, high pH can also promote metal precipitation, making it difficult to separate adsorption from precipitation. Natural waters contain competing ions such as bicarbonate, carbonate, sulfate and chloride. These ions may compete for reactive sites and alter contaminant speciation. Therefore, biochar performance observed in single-solute laboratory experiments may differ from its behavior in complex natural waters (Thomas et al., 2020).

Biochar Modification

Modification can improve the chemical selectivity and adsorption capacity of biochar. Physical activation increases accessible pores, while oxidation can introduce additional carboxyl and hydroxyl groups. Loading biochar with Fe, Mg, Al or Ca can create new reactive sites for nutrient and metal removal. Fe-modified biochar is particularly useful for phosphate capture because Fe-containing surfaces provide positively charged sites and strong phosphate-binding mechanisms. Ca- and Mg-rich biochars can promote phosphate precipitation, while surface oxidation can improve complexation with heavy metals (Zhang et al., 2020).

Conclusion

Biochar removes nutrients and heavy metals through a combination of chemical and physical processes. Ammonium is mainly retained through cation exchange and electrostatic attraction, whereas nitrate requires suitable positively charged surfaces. Phosphate removal is strongly associated with ligand exchange and precipitation involving Ca, Mg, Fe and Al. Heavy metals are retained through electrostatic attraction, ion exchange, surface complexation, precipitation and redox transformation. The effectiveness of biochar therefore depends not only on surface area but also on functional groups, mineral composition, surface charge, pH and contaminant speciation. Understanding these chemical principles is essential for designing modified biochars capable of efficiently controlling nutrient enrichment and heavy-metal contamination in aquatic environments.

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