Review

Phosphorus Removal from Wastewater: The Potential Use of Biochar and the Key Controlling Factors

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Abstract: In recent years, a large volume of literature has been published regarding the removal of phosphorus (P) from wastewater. Various sorbing materials, such as metal oxides and hydroxides, carbonates and hydroxides of calcium (Ca) and magnesium (Mg), hydrotalcite, activated carbon, anion exchange resins, industrial solid wastes and organic solid wastes, have been suggested for P removal. Many of these sorbents are expensive and/or may cause some environmental problems. In contrast, biochar, as an economical and environmentally friendly sorbing material, has received much attention in recent years and has been used as a novel sorbent for the removal of different organic and inorganic pollutants. Biochar is a type of sustainable carbonaceous material that is produced from the thermal treatment of agricultural organic residues and other organic waste streams under oxygen free conditions. This paper reviews the potential use of biochar and the key controlling factors affecting P removal from wastewater. The ability of biochar to remove P from wastewater depends on its physical and chemical properties. Some of the most important physicochemical properties of biochar (structural characteristics, electrical conductivity (EC), mineral composition, pH, zeta potential, cation exchange capacity (CEC) and anion exchange capacity (AEC)) are affected by the feedstock type as well as temperature of pyrolysis and the P sorption capacity is highly dependent on these properties. The P removal is also affected by the water matrix chemistry, such as the presence of competing ions and bulk pH conditions. Finally, several recommendations for future research have been proposed to facilitate and enhance the environmental efficiency of biochar application.

Keywords: phosphorus removal; biochar; pyrolysis; feedstock; sorption capacity

1. Introduction

In recent decades, with the rapid growth of industry, the intensification of agriculture and the increased production of wastewaters, eutrophication has shown to be a serious threat to aquatic ecosystems. Phosphorus (P) and nitrogen (N) in a lesser extent, are important nutrients for plant growth, and their aqueous concentrations influence the trophic status of aquatic ecosystems [1,2]. Among these two elements, phosphorus has been thought for a long time to be the most important in terms of nutrition, and plant growth can be controlled by controlling dissolved phosphorus concentration [1]. Therefore, it has been considered to be the key nutrient leading to the eutrophication of reservoirs and lakes [3]. Water eutrophication is a critical environmental problem throughout the world today (it occurs when P concentrations is higher than a concentration ranging from 0.003 to 0.8 µg/L) [4,5]. Phosphorus enters the aquatic environment from a variety of sources (both point and nonpoint sources) and mainly includes urban and domestic wastewater, agricultural activities through the excessive use of chemical fertilizers, development of...
industrial plants and discharge of industrial wastewater, mining activities, discharge of livestock manure and aquaculture baits [6] (Figure 1). Phosphorus presence in excess in aquatic ecosystems has been reported to favor the occurrence of toxic species of phytoplankton in algal efflorescence [7]. These toxic microalgae and cyanobacteria pose a threat to human and animal health in several countries [8–10].

Chemical characterization of wastewater is an important factor in determining its potential negative effects on ecosystems [11] (Table 1). Due to the type of human activity, there are different types of wastewater, including (i) Composites textile industries (pH: 5.5–11.0); (ii) Textile processing industries (pH: 7.0–8.5); (iii) Woolen industries (pH: 7.0–11) [12].

Table 1. Wastewater types with their pH and phosphorus concentration.

| Wastewater Type                  | pH Range | P Forms (mg/L) | References |
|---------------------------------|----------|----------------|------------|
| Swine wastewater                | 7.8      | 84 (P-PO₄³⁻)   | [14]       |
| Sewage wastewater               | 6.3–7.3  | Approximately 4–8 (organic and inorganic P) | [15,16] |
| Domestic/Municipal wastewater   | 7–8      | 4–15 (P-PO₄³⁻) (P-soluble: 11 and P-suspended: 4) | [17] |
| Municipal/Industrial Wastewater | 4.4–11.1 | 1.5–3.5 (Total P) | [18,19] |
| Piggery wastewater              | 6.64 and 8.1 | 4.2 (P-PO₄³⁻) | [20,21] |
| Swine wastewater                | 6.37–7.62| 24.1 mg/kg (as orthophosphate) | [22–24] |

Almost all phosphorus is reported to be in the form of orthophosphate ions (H₂PO₄⁻, HPO₄²⁻, PO₄³⁻) in natural water and wastewater. In many studies, total phosphorus has been used as a quantitative indicator in wastewater, while all forms of phosphorus do not have the same mobility and availability. Thus, the amount of total phosphorus does not indicate the value of its effective concentration. Phosphorus fractionation is influenced by inorganic and organic forms and different ions in the wastewater (for example the forms

Figure 1. Different P sources to water resources and its consequences on water quality at high P concentration (free photograph from Nemery [13], Phosphorus and eutrophication, Encyclopedia of the Environment, [online ISSN 2555-0950] url: https://www.encyclopedie-environnement.org/en/water/phosphorus-and-eutrophication/) (accessed on 7 February 2021).
associated with oxides and hydroxides of Aluminum (Al), Iron (Fe), Manganese (Mn) and Calcium (Ca)). The available form of phosphorus in wastewater is determined by Soluble Reactive Phosphorus (SRP) and the ratio of orthophosphate to SRP [25–27]. Phosphorus compounds are changed to orthophosphate solution after hydrolysis and biodegradation in wastewater [28]. Orthophosphate is an essential and available form of phosphorus for organism growth in aquatic ecosystems [29].

Globally, much attention has been paid to improve the methods of wastewater treatment and P removal. To control eutrophication, the United States Environmental Protection Agency (USEPA) has recommended that total P should not exceed 0.05 mg P/L in a stream at a point source where it enters a lake or reservoir and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs [30,31]. The Australian and New Zealand water quality guidelines recommend that Australian upland rivers, depending on the region, should have a total P concentration < 0.01–0.02 mg P/L, low land rivers < 0.005–0.01 mg P/L, freshwater lakes and reservoirs < 0.01–0.025 mg P/L and estuaries < 0.02–0.10 mg P/L [32].

Therefore, it is essential to choose a method that is nature-friendly and has a good efficiency in terms of phosphorus removal. Biochar (carbon-rich material) is an important and effective adsorbent used to remove a wide range of pollutants in aqueous solutions [6,33]. The benefits of biochar application as an adsorbent are listed as follows:

- Commercial and environmental [34];
- Renewable energy sources [35];
- Rapid sorption [36];
- Decrease the threat associated with pollutants [37].

The use of the recovered phosphorus form is economically viable for the plant and does not limit the use of some P chemical fertilizers [38].

Biochar is charcoal that is produced by pyrolysis of organic materials in an oxygen-free condition. Biochar is often used for water and wastewater treatment because of its high specific surface area and sorption capacity, high internal microporosity, abundant functional groups, low cost and easy availability [33,39–42]. The active carbon functional groups include phenolic (hydroxylic), carbonyl, carboxylic, ether etc. The number and type of these functional groups depending on the chemical and heat treatment of the carbon source [43]. Chemical processes principally control P sorption onto biochar use because it is rich in organic functional groups [14].

The most important factors affecting biochar characteristics are the properties of feedstocks and pyrolysis temperature treatment conditions [35].

Some studies have suggested that biochar may be pre-treated to produce biochar composites [44]. Pre-treatment increases functional groups density in biochar (aluminum ion bound to the carboxylic groups of the biochar) or surface-active sites (nanoparticles sorbed onto biochar). It is an amendment for carbon sequestration and improving soil fertility [45]. Proper soil fertility improves plant growth and nutrients accumulated during treated wastewater irrigation [46]. Additionally, biochar has been reported to increase microbial P biomass and microbial activity [47].

According to the above-mentioned aspects, the effect of biochar on phosphorus removal from wastewater has not been systematically reviewed, while phosphorus is an important nutrient and environmental pollutant when leached into water and wastewater systems. There is an urgent need to provide a literature overview regarding the effects of biochar on phosphorus removal in wastewater systems and to recommend areas for future research. Therefore, the aim of this paper is to present a review to describe the P removal efficiency, sorption mechanisms of biochar use in P removal and the factors affecting the sorption mechanisms of P onto biochar. Additionally, it focuses on the latest studies dealing with the use of biochar as sorbents or amendments for removing P from wastewater treatment processes.
2. The Importance of Biochar Application Compared to Other Methods

A large volume of literature has been published regarding the removal of P from wastewater, aqueous solutions, sewage sludge and manure. Usually, the selection of a P removal method largely depends on the characteristics of the wastewater, and the choice of the method has a great impact on the generated products and P removal efficiency. In brief, biological, chemical and physical methods are applied for P removal from wastewater (Table 2). These methods are suggested for P removal treatment technologies at smaller scales, because P releases from small treatment systems may have a greater environmental impact than previously believed [48].

### Table 2. Overview of the main P-removing methods.

| Methods | Description | References |
|---------|-------------|------------|
| Biological | Biological P removal (i.e., Enhanced Biological Phosphorus Removal (EPBR)) with activated sludge systems is based on the biochemical process coupled to the luxury P-uptake, which relies on phosphorus-accumulating organisms (PAO). | [49,50] |
| Chemical | The most common chemical P removal approaches involve dosing metal salts (i.e., aluminum or iron salts) to either pre-treated wastewater, activated sludge reactors or at the outlet of secondary clarifiers | [49] |
| Physical | Use of reactive media filters which rely on P-sorbing properties of some materials such as natural products (e.g., apatite, bauxite or limestone), industrial waste products (e.g., fly-ash, ochre or steel slag) or man-made products (e.g., Filtralite™). | [51] |

The biological removal of P is dependent on phosphorus-accumulating organisms (PAO) that are capable of accumulating P in excess of metabolic requirements (luxury uptake) [52]. Various organisms, such as fungi, algae and bacteria, have also been suggested for biological P removal [52,53].

In general, physical methods, such as membrane filters and reverse osmosis, are very expensive and not much applied for this specific purpose, while chemical methods, such as the addition of dissolved salts of Al, Fe and Ca, induce sludge production and effluent neutralization, and thus are not recommended. The efficiency of P removal by biological methods can be as high as 100%; however, these methods are less effective on low P levels because the low P content is not sufficient for the metabolism of microorganisms. In addition, biological methods require specific care and strict control. The absence of carbon sources and microorganism culturing are limited factors for this method [54].

The use of sorption technology is very attractive and effective because it has high efficiency and does not produce sludge [55]. Many sorbents for P removal have been tested by researchers and it has been suggested that they mainly have high porosity, high internal surfaces and high content of Al, Fe, Ca and magnesium (Mg) or have locations suitable for P anion exchange [56]. Some of the sorbents used in the research for P removal include: clay minerals [57], zeolites [58], Al oxides [59], limestone [60], fly ash [61], steel slag [62] and biochar [63]. There are various challenges with this method that may limit its use. The most important challenge regarding the sorption method is the capacity of the adsorbents, which may be limited and insufficient for sorption [64]. This challenge can be solved by the adsorbent replacement, but usually, the sorbent regeneration method is used to reduce costs. In general, the use of modified adsorbents with high sorption capacity (such as biochar) is an appropriate strategy to reduce process costs.

Compared to chemical and biological methods, the sorption method (as a physical method) has received much attention due to its low cost, simplicity of operation, high efficiency and high sorption rate, especially at low P levels (Figure 2).
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Figure 2. Advantages of biochar application over other phosphorus removal methods.

Figure 3 provides an overview of the variety of useful organic materials (biochar types) used to remove phosphorus from wastewater and its role in sustainable development.
3. Other Suggested Adsorbents along with Biochar

The general framework for P removal from wastewater may include pre-treatment processes that remove P from the bulk material and accumulate in a separate stream for subsequent treatment. About 25% of phosphorus in the waste streams can be removed by immobilization on a solid sorbent [65]. Low sorption efficiency, and secondary pollution are difficulties to single biochar application for P removal [66]. Some nano-particles materials may be involved in the removal of organic pollutants (through activation of hydrogen peroxide and persulfate) [45] along with the use of biochar for phosphorus removal from wastewater. Lignocellulosic biomass, physical activation and slow pyrolysis [35] are important components for the production of efficient P removal biochars.

Many adsorbents with biochar have been used to remove P from wastewater and aqueous solutions, including inorganic and organic adsorbents. Some of these adsorbents are shortly introduced in the subsequent sub-sections.

3.1. Metal Oxides and Hydroxides

Oxides and hydroxides of Fe, Al, manganese (Mn) and titanium (Ti) are used to remove cationic and anionic pollutants from water and wastewater [67]. The predominant mechanism of P sorption on oxides and hydroxides is ligand exchange by the formation of inner-sphere complexes [68]. Some researchers have suggested that metal oxides and hydroxides can be effective adsorbents for P removal and removal yield ranging from 10–100% have been reported [69–72].
3.2. Carbonates and Hydroxides of Calcium and Magnesium Cations

The mechanism of P removal by these sorbents is usually by precipitation of Ca and Mg phosphates. The partial dissolution of Ca and Mg carbonates in aqueous solutions releases Ca and Mg cations, thereby combining these cations with P about 10 mg PO$_4$$^-$$^3$ per g solid to form Ca and Mg hydroxyl phosphates [51,73].

3.3. Hydrotalcite

Hydrotalcite is a group of clays that are synthesized in the laboratory. These clays are composed of positively charged sheets that are neutralized by interlayer anions [74]. Mechanisms of sorption of various anions, such as phosphate (around 91 mg P per g), by these synthetic clays include surface sorption, interlayer anion exchange and surface precipitation [75–77].

3.4. Anion Exchange Resins

Ion exchange resins are an important group of ion exchangers that are used to remove cationic and anionic pollutants from water and wastewater. Anion exchange resins with a positive charge are used to remove phosphate (phosphate removal higher than 95%) from aqueous solutions [78–80].

3.5. Industrial Wastes

The use of some industrial wastes as adsorbents can reduce landfill costs and prevent soil contamination. Many industrial wastes have been used to remove various contaminants, such as P. The methods and efficiencies of P removal by these materials depend on their physical and chemical properties. They are usually made of oxides, hydroxides or carbonates of Al, Fe, Mg and Ca. Thus, the predominant mechanisms for P removal by these materials are ligand exchange and surface precipitation. Red Mud [81–84], fly ash [85,86], Fe oxide tailing materials [87], bauxite [88] and steel slags [89,90] are some of the materials that have been used as P adsorbents in research.

3.6. Organic Wastes

Organic wastes are often of agricultural origin and are used as inexpensive sorbents to remove P contamination from water and wastewater. Some of these agricultural wastes mentioned in the research are: wheat straw [66], soybean hulls [91] and pine cone [92].

3.7. Hydrochars

Hydrochars is made by hydrothermal carbonization at low temperature (by 300 °C) in the subcritical water of wet solid materials, i.e., slurry and organic, which displays a sorption capacity of 15 mg PO$_4$$^-$$^3$ per g of hydrochar [93,94]. Due to the existence of functional groups, it can remove polar organics, pathogens and inorganic contaminants such as anions and cations from wastewater [94]. Even if hydrochar mostly harbors negative charges, it is suitable to be an adsorbent for cations [95], but can still contribute to anionic compounds removal such as phosphate anions [96].

4. The Most Important Factors Affecting the Sorption of P by Biochar

4.1. Biochar Surface Area

Generally, as the pyrolysis temperature increases, the pore structure of biochar develops, and as a consequence, its specific surface area increases [97]. Removal of P by biochars is often accomplished through the sorption process and the development of the biochar surface area improves the transfer of P from the solution to the sorbent surfaces. Most studies have shown that increasing the pyrolysis temperature to a certain threshold increases the biochar surface area, but some findings have reported that the biochar pore structure collapses at very high temperatures. The degradation of the biochar surface area at high temperatures consequently reduces its sorption capacity [98,99].
4.2. Influence of Metal Oxides on the Sorption of P by Biochar

Many studies have shown that biochars contain a variety of metal oxides of Fe, Al, Ca, Mg etc. The presence of metal oxides increases the sorption of P by biochar. Phosphate in aqueous solutions with these metal oxides forms a precipitate through weak hydrogen bonds. Phosphate may also precipitate by reacting with these metal oxides through chemical reactions and strong chemical bonds [100]. Various studies have investigated the sorption of P by different types of biochars and the results have shown that biochars with higher Ca and Mg content have higher P sorption [96,98,101–103]. Due to the enhanced density of hydroxyl functional groups, an increasing P sorption by composite biochars has been reported. Therefore, chemical pretreatments with increasing metal cation concentrations are performed prior to the preparation of biochar. Different types of biochars are treated by the incorporation of biomass and Mg, Ca, Fe and Al salts for 2–12 h before pyrolysis [104–106].

4.3. The Effect of Coexisting Bulk Solution Anions on the Sorption of Phosphorus by Biochar

In most cases, aqueous solutions or wastewater in addition to P contain other anions and cations. Therefore, when determining P sorption, the presence of these ions may affect the sorption processes, and the amount of P sorbed. In some studies, the influence of coexisting anions on the sorption of P by biochar in synthetic solutions or in real wastewater has been investigated. The results of these studies show that the presence of organic and inorganic anions (for example Cl\(^-\), NO\(_3^-\) and HCO\(_3^-\)) in aqueous solutions decrease the P sorption by biochar [14,101,107]. The decrease in P sorption in the presence of coexisting anions may be due to two reasons: (i) competition between coexisting anions and P for the occupation of the sorption sites and (ii) when coexisting anions react with biochar surfaces, they may form precipitates, thus occupying sorption sites and blocking biochar pores [14].

4.4. Influence of Feedstock Types and Pyrolysis Temperature on Removal of Phosphorus from Wastewater and Aqueous Solutions

The biochar physicochemical properties are influenced by feedstock type, pyrolysis temperature and pre-treatment methods; all of them significantly affect the biochar capacity to remove P [6]. In addition to the feedstock type and temperature of pyrolysis, the most important properties of biochars that may affect P sorption capacity include pH, electrical conductivity (EC), CEC, AEC, total acidity, carbon chemistry, metal composition (Ca, Mg, K, Fe, Al, etc.), surface area, porosity and functional groups density and identity [6,96–98,100,104,108–120]. The P sorption capacity of various biochars can, therefore, be affected by a range of physical, chemical, and structural properties that may exert a synergistic effect [120]. Briefly, different types of biochar produced from different biomass sources, different pre- and post-treatment methods and different pyrolysis temperatures have been reported in the literature to affect P removal efficiency from wastewater and aqueous solutions (Tables 3 and 4). Depending on the biochar type, the amount of phosphorus removed from the wastewater can even reach up to 600 mg·g\(^{-1}\) through various sorption mechanisms (Table 3). According to Table 3, several studies showed that biochar can reduce water soluble phosphorus by 20 to 90%. Nowadays, the use of modified biochars has shown to be more effective than non-modified biochars.

The enormous diversity of feedstock biomass, as well as the various technologies of thermochemical decomposition of feedstock (high/low temperature pyrolysis, carbonization, gasification, etc.), influences the quality of final biochar and leads to highly diverse chemical (carbon content, composition, and content of other elements, the content of functional groups) and physical properties (e.g. specific surface area, structure, pore geometry) [140].
Table 3. P removal efficiency and sorption mechanisms by different biochar types.

| Sorbent                                                                 | Amount of PO₄-P sorbed (mg g⁻¹) | Sorption Mechanisms                                                                 | References |
|-------------------------------------------------------------------------|----------------------------------|-------------------------------------------------------------------------------------|------------|
| La(OH)₃-modified magnetic pineapple biochar                             | 101.2                            | Precipitation, electrostatic interaction, ligand exchange, inner-sphere complexation | [121]      |
| Pineapple biochar (the ratio between lanthanum and magnetic biochar is 10 mmol/g in the suspension) | 3.7                              | Not reported                                                                        |            |
| Bamboo biochar modified with a-Fe₂O₃/Fe₂O₄                              | 2.8                              | Not reported                                                                        | [122]      |
| Bamboo modified with varying amount of Mg-Al and Mg-Fe (3:1) layered double hydroxide | 32                               | Interlayer anion exchange, surface sorption, precipitation Ligand exchange, electrostatic attraction | [123]      |
| Mg laden bamboo biochar synthesized at 400, 500 and 600 °C              | 370                              | Detailed mechanisms Not reported                                                   | [117]      |
| A novel combined electrochemical MgO biochar (prepared from brown marine macroalgae) | 600                              | Ligand exchange, electrostatic attraction Surface electrostatic, Mg²⁺ precipitation, complexation with hydroxyl functional groups | [104]      |
| Brown marine macroalgae (unmodified biochar)                            | 5                                | Not reported                                                                        | [124]      |
| Iron modification waste activated sludge-based biochar                  | 111                              | Ligand exchange, sorption on active site, precipitation with Mg ions                | [125]      |
| Mg-loaded biochar from different feedstock (Tarto straw, Corn straw, Cassava straw, Chinese fir straw, Banana straw, Camelia oleifera shell) | 31.2                             | Electrostatic attraction, surface complexation, anion exchange                     | [126]      |
| Vegetable biochar/Mg-Al layered double oxide                             | 132.8                            | Precipitation                                                                        | [127]      |
| Calcium doped biochar produced from biosolids                            | 147                              | P-OH bonding                                                                         | [128]      |
| Biochar from waste-derived fungal biomass (Magnetic biochar)            | 23.9                             | Sorption on active site, precipitation with Mg ions                                  | [129]      |
| Biochar derived from magnesium-pretreated cypress sawdust (pyrolysis temperature 400 °C) | 19.2                             |                                                                                     |            |
| Biochar derived from magnesium-pretreated cypress sawdust (pyrolysis temperature 600 °C) | 33.8                             |                                                                                     |            |
| Nano Ca-Mg loaded biochar                                               | 326.6                            | Not reported                                                                         | [130]      |
| Iron modified corn straw biochar                                         | —                                | Precipitation, Fe-O-P-P-C bonds                                                     | [131]      |
| Nano-rod Ca-decorated sludge derived carbon                             | 116.8                            | Precipitation as hydroxyl apatite                                                   | [132]      |
| Wood and sewage sludge derived biochar pyrolyzed at various temperature | 0.7–1.2                          | Not reported                                                                         | [120]      |
| Magnesium alginate/chitosan modified biochar microspheres from Thalia dealbata | 46.5                             | Precipitation with minerals, ligand exchange                                         | [133]      |
| Sesame straw biochar produced at different pyrolysis temperature (300, 500 and 700 °C) | 3.45–34.2                      | Not reported                                                                         | [6]        |
| Maize-Straw biochar (unmodified)                                         | 8.8                              | Not reported                                                                         | [134]      |
| Pine biochar (unmodified)                                                | 13.9                             | Repulsion forces between biochar surface and phosphate ion cause of the low adsorption | [135]      |
| Pine sawdust biochar                                                    | 2                                |                                                                                     |            |
| Wheat straw biochar with HCl activated and coated with FeCl₃·6H₂O       | 16.6                             | Not reported                                                                         | [136]      |
Table 3. Cont.

| Sorbent                                      | Amount of PO$_4$-P sorbed (mg g$^{-1}$) | Sorption Mechanisms                                                                 | References |
|----------------------------------------------|-----------------------------------------|------------------------------------------------------------------------------------|------------|
| Calcium Flour biochar                        | 314.2                                   | Reaction of Ca(OH)$_2$ and PO$_4$ forming the hydroxylapatite                      | [137]      |
| Cotton stalk solid waste                    | 50                                      | Precipitation with Ca, Mg ions                                                    | [138]      |
| Biochar derived from digested sugar beet tailing | 25                                      | Main sorption sites: Colloidal and nano sized MgO (particles) on the biochar surface | [101]      |
| Biochar/MgAl-LDH fine composite             | 350                                     | Surface sorption, interlayer exchange                                             | [111]      |
| Unmodified biochar (different feedstock)    | 0–30                                    | Precipitation with Mg and Ca ions                                                  | [96]       |
| Biochar derived from Peanut shell           | 3.8                                     | Not reported                                                                        | [98]       |

Table 4. P removal efficiency (%) of modified-biochar materials applied on different wastewater type.

| The Main Description                                                                 | Percentage | Feedstock Biochar/Solution Type/Treatment pH Range | References |
|-------------------------------------------------------------------------------------|------------|-----------------------------------------------------|------------|
| Calcium-rich biochars for P removal from wastewater                                 | ≈80        | Calcium-rich biochars (pyrolysis of crab shell)/30 mL KH$_2$PO$_4$ solution (80 mg P/L) and biogas effluent of swine manure wastewater (11.59 mg P/L)/11.25–14 | [63]       |
| Lightweight expanded clay aggregates (LECA) along with biochar and plant increased P removal from wastewater compared to (LECA + plants) | 22.5       | LECA + with biochar + plant/wastewater in horizontal subsurface flow constructed wetlands (water quality 12.4–17.5 mg/L P-PO$_4$)/6.7–7.1 | [139]      |
| The Mg/biochar is more effective than biochar in P removal                           | 90         | Magnesium (Mg) Modified Corn Biochar/swine Wastewater (84 mg/L P-PO$_4$)/3–11 | [14]       |
| Core-shell γ-Al$_2$O$_3$/Fe$_3$O$_4$ biochar for P removal                           | 91         | Core-shell γ-Al$_2$O$_3$/Fe$_3$O$_4$ biochar/aqueous phosphate solutions (10–500 mg/L NaH$_2$PO$_4$)/3–11 | [66]       |
| Peanut shell-derived biochar is as an alternative and renewable sorptive media for phosphate removal | 61         | Peanut shell-derived biochar/aqueous phosphate solution (5.0 mg/L using KH$_2$PO$_4$)/7 | [98]       |

Zhang et al. [114] investigated the sorption of P by biochars (one natural woody biochar and eight manufactured plant-derived biochars) prepared from different feedstocks and at different temperatures. Their results showed that among the nine biochars studied, only biochar derived from Mallee (*Eucalyptus polybractea*) produced at 720 °C with a solid residence time of 20 min showed a high P retention ability. Results from the kinetic study of P sorption on Mallee biochar indicated that there were two stages in P sorption on Mallee biochar, a rapid chemisorption stage followed by a surface-diffusion controlled stage when the surface sorption sites were saturated. Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy and attenuated total reflectance-Fourier transform infrared spectroscopy revealed that calcium carbonate was mainly responsible for P chemisorption on Mallee biochar.

Zhou et al. [118] investigated the P sorption capacities of different biochars made from plant waste, including rice straw, *Phragmites communis*, sawdust, and eggshell exposed to a range of pyrolysis temperatures (300, 500 and 700 °C). Their results indicated that the effect of pyrolysis temperature on the physiochemical properties of biochar varied with feedstock material. Biochars derived from plant waste had a limited sorption capacity or even released P, but sorption of P could be improved by adjusting pyrolysis temperature.
The maximum adsorption of P on rice straw, *Phragmites communis* and sawdust, produced at pyrolysis temperatures of 700, 300 and 300 °C, was 5.41, 7.75 and 3.86 mg g⁻¹, respectively. Eggshell biochar can adsorb P, and its sorption capacity increased with an increase in pyrolysis temperature. The less negative charge and higher surface area of eggshell biochar enabled higher P sorption capacity.

### 4.5. Structural Characteristics

The biochar structural properties that may affect P sorption include the distribution of pore size, specific surface area and particle size. The differences in structural properties derive from the differences in the original feedstocks and conditions of pyrolysis [120].

The development of a biochar specific surface area provides a large space for contaminants’ sorption and certainly increases the interaction between contaminants and biochar. In general, as the pyrolysis temperature increases, the pore structure and specific surface area of the biochar increases [97]. The expansion of the pore structure and large surface area of biochar provides ample space for P sorption. Increasing the specific surface area of biochar at high temperatures is due to the release of numerous volatile substances from the biomass structure. However, parts of the porous structure will be collapsed at very high temperatures and the pores will be blocked, which will eventually reduce the active sites of sorption [6]. In addition, under the same pyrolysis temperatures, different types of biomass exhibit different surface areas [141].

Brendova et al. [140] investigated the pyrolysis temperature and type of feedstock on the composition of biochar pores. The most important properties that affected the composition of the biochar pores were pyrolysis temperature, lignin and ash contents. As the temperature of pyrolysis and lignin increased, the volume of micropore increased.

Jung et al. [104] reported that increasing the pyrolysis temperature from 200–400 °C increased surface area and P sorption capacity of biochar. However, when the pyrolysis temperature was higher than 400 °C, the specific surface area and P sorption capacity of biochar decreased.

Increasing the specific surface area and porosity of biochars prepared from different types of feedstock was carried out by activation with CO₂ at 800 °C and the P sorption significantly improved. However, no correlation was observed between the biochar-specific surface area and P removal even after activation [120].

### 4.6. Electrical Conductivity (EC)

Very little work has been done on the effect of the EC of biochars derived from different feedstock types on P sorption. Dugdug et al. [116] found that the EC of willow wood biochar was three times higher than that of hardwood and wheat straw biochars. Additionally, the P sorption by willow wood biochar was higher than other biochars, indicating that soluble salts can cause extra sorption of P.

Jun et al. [142] also indicated that P sorption by saline soils was three times higher than that of artificial control soils. The mechanism for that action is not clear but may be due to the possible precipitation of PO₄-P with Ca and Mg in the saline condition.

### 4.7. Metal Composition

The types of feedstock used for biochar production have metal cations dispersed within their bulk structure. Pyrolysis and activation conditions expose these metals to surfaces and make them available to react [120].

The results of Melia et al. [120] showed that the content of Ca and Mg were significantly correlated with the P sorption in unmodified biochar (12 biochar tested). They also investigated the effect of pyrolysis temperature (550 and 700 °C) on the sorption of P by biochar. Their results showed that biochar prepared at 700 °C was less capable of sorption of P; in contrast, these biochars have a higher content of metal cations (Ca, Mg, Fe and Al), indicating that properties other than the content of metal cations were important in the sorption of P by biochar, and the speciation of metals in the biochar structure plays a key role.
role in the sorption of P. In general, their findings suggested that for effective P retention and sorption, the best approach is to use a low pyrolysis temperature and to increase the Ca and Mg concentrations of biochar. A possible mechanism of P removal in the presence of metal cations is the formation of weak hydrogen bonds (surface deposition) and strong chemical bonds (precipitation) [6,100].

Hollister et al. [143] reported that original oak biochar adsorbs more P than water-extracted oak biochar, indicating that the metal cations present in the biochar structure provide P sorption sites but are washed with cold water during extraction.

Jung et al. [98] tested different types of biochars (oak wood, bamboo wood, maize residue, soybean stover and peanut shell) to remove P from aqueous solutions, and their results showed that peanut shell biochar had the best performance for P removal due to its high Ca and Mg content.

Shepherd et al. [115] studied the mechanisms of P sorption by anaerobically digested sewage sludge/ochre derived biochar and found that P interaction with Fe minerals in the biochars tested was crucial for enabling P sorption.

Yao et al. [101,112] reported that sugar beet tailings and engineered tomato biochars had a high performance for P sorption due to their high Mg content (10% and 2%, respectively). The reason for the high sorption capacity of P is the high point of zero charges of pH ($\text{pH}_{\text{pzc}} = 12$) of MgO. MgO has a positive charge at a pH of less than 12 and adsorbs P through electrostatic bonding. In addition, parts of the MgO dissolves in the solution, and the chemical reactions (precipitation) that occur between Mg and P cause the P to be removed.

4.8. pH

Solution pH, biochar pH and $\text{pH}_{\text{pzc}}$ may also be effective for the speciation of P in the solution, and thus, on its sorption by the biochar. Solution pH and $\text{pH}_{\text{pzc}}$ of biochar are key parameters that influence the changes of biochar surface charge and P sorption.

Jung et al. [99] reported that the $\text{pH}_{\text{pzc}}$ value of biochars at pyrolysis temperature of 400 °C was higher than the solution pH that caused $\text{PO}_4^{3-}$ to be adsorbed on the positively charged biochar by electrostatic sorption. Biochar prepared at 200 °C showed a small P sorption capacity because the biochar surface charge is close to zero when the solution pH is 7.

DugDug et al. [116] investigated the P sorption capacity of willow wood, hardwood and wheat straw biochars, and their results showed that willow wood biochar had higher P sorption capacity compared to hardwood and wheat straw biochars because of its higher pH. They suggested that a higher pH of willow wood enables the appropriate conditions for the interaction of P and precipitation of P with other ions, such as Ca$^{2+}$ and Mg$^{2+}$.

Mukherjee et al. [144] stated that the $\text{pH}_{\text{pzc}}$ of biochars varies depending on the type of biochar between 2.0 and 3.5, which means that the biochar surfaces have no charge between these values, but will have a negative charge when the pH is greater than 3.5. A study by Shepherd et al. [115] showed that biochar charge was negative at pH greater than 3. In addition, the anion exchange capacity on biochar surfaces often occurs in acidic pH. Thus, by increasing the pH of the solution to more than 3, the biochar will have a negative charge that will repulse negative ions, such as P anions.

Species of $\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$ and $\text{PO}_4^{3-}$ are the four possible species of inorganic P in aqueous solutions, with their speciation determined according to different pKa values and bulk pH conditions. Generally, the sorption-free energy of $\text{H}_2\text{PO}_4^-$ is lower than that of $\text{HPO}_4^{2-}$, which indicates that the sorption of $\text{H}_2\text{PO}_4^-$ by biochar is easier. Phosphorus sorption at the high pH of the solution is strongly reduced because the dominant species of $\text{PO}_4^{3-}$ is hardly adsorbed on the biochar surfaces, and $\text{PO}_4^{3-}$ competes with OH$^-$ to fill the sorption sites [6,98,145].
4.9. Zeta Potential

The surfaces of biochars and carbon-based materials are often negatively charged and hardly adsorb negative ions [101]. Zeta potential is one of the factors affecting the type (negative or positive) and amount of charge on the biochar surfaces. High values of zeta potential of biochar indicate that the biochar surfaces are positively charged and the biochar will be able to adsorb P ions.

Jung et al. [98] investigated P sorption by biochars obtained from different feedstock (oak wood, bamboo, maize residue, soybean stover and peanut shell) and their results showed that biochars with higher zeta potentials had higher P sorption.

A study by Yao et al. [101] on undigested and anaerobically digested sugar beet tailings biochars confirmed that these biochars had negative zeta potentials, indicating that they would be negatively charged in neutral conditions. Anaerobically digested sugar beet tailings biochar showed higher zeta potential than undigested sugar beet tailings biochar, so it was expected that the sorption of P by anaerobically digested sugar beet tailings biochar was higher.

Zhang et al. [102] found that the pristine biochar surface is negatively charged, and thus, cannot easily absorb the negatively charged P. Plant-derived biochar used in the study of Zhou et al. [118] had a low zeta potential (−16.6 to −41.9 mV), meaning that electrostatic repulsion between the negatively charged surface sites and electronegative P species resulted in the lower P sorption.

Feedstock type and pyrolysis temperatures are the parameters that influence the zeta potential of biochar and there is little research in this subject.

4.10. CEC and AEC

In general, the CEC of most biochars is high and they tend to attract cations [146]. The amount of CEC varies widely depending on the feedstock type and production conditions (such as pyrolysis temperature).

Banik et al. [147] studied the influence of feedstock type and temperature of pyrolysis on some properties of biochar such as CEC and AEC. Their results indicated that biochars produced at ≤500 °C have high CEC and low AEC due to the dominance of negative surface charge arising from carboxylate and phenolate functional groups. Biochars produced at ≥700 °C have low CEC and high AEC, consistent with a dominance of positive surface charge arising from nonhydrolyzable bridging oxonium (oxygen heterocycles) groups.

Acidic functional groups and basic functional groups provide cationic and anionic exchange sites, respectively. Pyrolysis temperature can affect the type and amount of functional groups as well as the biochar’s capacity for ion exchange [6]. Zhang et al. [111] reported that when pyrolysis temperatures decrease, the amount of acidic functional groups increases. Nguyen and Lehmann [148] suggested that when pyrolysis temperature increased from 300 °C to 600 °C, half the amount of the carboxyl groups in corn and oak biochars decreased.

5. P sorption Thermodynamic and Mechanisms in Biochar

Biochar has special physico-chemical characteristics, such as a high surface area, high porosity etc., that recovered P from wastewater; therefore, it is important to study the sorption mechanisms, kinetic models and thermodynamics to recognize the nature of the sorption process in biochar.

Kinetic model types, including the pseudo-first-order, pseudo-second-order and intraparticle diffusion models, may provide insights regarding the P sorption mechanisms in biochar. Several studies showed that pseudo-first-order is the best model implying P physical sorption [118,137,149]. Pyrolysis temperature is a factor known to improve P sorption. Zeta potential, total volume, specific surface area and pH are increased at a pyrolysis high temperature. The maximum sorption of P is obtained at high pyrolysis temperature (700 °C > 300 °C). Models behave differently in several temperatures and types of biochar raw materials [118].
Generally, the P sorption process is an endothermic reaction in biochar ($\Delta G < 0$, $\Delta S > 0$ and $\Delta H > 0$). Isotherms including Freundlich, Langmuir and Langmuir-Freundlich are able to predict the phosphorus sorption onto biochar from wastewater [118]. Langmuir usually has a better fit with experimental data in these conditions [150]. The various mechanisms of phosphorus sorption on surfaces are summarized in Figure 4. The different sorption mechanism displayed in Figure 4 indicate the amount of P sorbed on the surface of biochar varies according to the chemical conditions of the bulk solutions. Some mechanisms immobilize phosphorus on their surface with high affinity and strength (e.g., ligand exchange and inner sphere bidentate) and some others with less strength (e.g., outer sphere complexation and electrostatic attraction) that decreases phosphorus removal efficiency.

Figure 4. Potential mechanisms for P sorption onto biochar surface (M: metal cation).

6. Conclusions, Perspectives and Future Direction

Biochar is an effective and environmentally friendly sorbent that can be used to remove P from aqueous solutions and wastewater. The physical and chemical properties of biochars greatly affect their ability to sorb phosphorus. Physical and chemical properties of biochars depend on the type of biomass, pre-treatment methods and pyrolysis conditions. Due to its high porous space as a physical sorbent, biochar displays high efficiency at different phosphorus concentration level. The use of this physical sorbent is low cost and prevents environmental problems. The most important properties of biochars that may be affected by the feedstock type and temperature of pyrolysis include biochar pH, EC, CEC, AEC, total acidity, carbon chemistry, metal composition (Ca, Mg, K, Fe, Al etc.), surface area, porosity, type and density of functional groups. In general, the sorption of P by biochar is controlled by various physical and chemical mechanisms. The physical sorption is related to the structure and surfaces of the biochar, and the chemical sorption depends on the type of biochar, the number and type of functional groups and the chemical composition of the biochar. Many studies have shown that the development of structure and surface area of biochar can improve P sorption capacity by providing sufficient space for the interaction of P and biochar surfaces. The phosphorus sorption often depends on the amount and type of metal cations available on the biochar surface because the predominant mechanism of P sorption on the biochar is usually through chemical precipitation. One way to increase the sorption capacity of biochars is to modify the adsorbent by various methods. Before biochar modification, evaluation of the controlling factors including choice of biochar modification and preparation technique, pyrolysis temperature, choice of chemical reagent,
pollutant properties and aqueous bulk conditions such as pH and wastewater composition is essential.

To facilitate the application of biochar for environmental purposes, several specific issues need to be investigated:

1. Development of biochar modification methods by salts of different metallic cations and determination of effective and efficient methods for removal of P from wastewater.
2. Evaluation of the stability of biochar after removal of P and determination of P retention by biochar.
3. Determination of P release from biochar surface by different extractors and application of biochar as soil P release fertilizer.
4. Evaluation of P removal efficiency by biochar in real or simulated wastewater.
5. A study of biochar recovery methods to reduce costs and reuse in wastewater treatment.
6. A study of multiple activation/treatment methods of biochar to increase the P sorption capacity.
7. An investigation of the relationship between types of metal cations and pyrolysis temperature to better understand the mechanisms of P sorption by biochar.
8. A precise and in-depth study of the mechanisms involved during P removal has yet to be published. Thus, P sorption mechanisms need to be studied to enable the development of more effective methods for producing biochars and optimizing their efficiency for practical application.

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