

Review

Biochar-Based Phosphorus Recovery from Different Waste Streams: Sources, Mechanisms, and Performance

Hai Bang Truong ^{1,2}, Thi Cuc Phuong Tran ^{3,*}, Thi Phuong Nguyen ³, Thi Thao Nguyen Nguyen ³, Doan Thi Oanh ⁴, Duong Thi Thuy ⁵ and Xuan Cuong Nguyen ^{6,7,*} 

- ¹ Optical Materials Research Group, Science and Technology Advanced Institute, Van Lang University, Ho Chi Minh City 700000, Vietnam; truonghaibang@vlu.edu.vn
 - ² Faculty of Applied Technology, School of Technology, Van Lang University, Ho Chi Minh City 700000, Vietnam
 - ³ Faculty of Environmental Engineering Technology, Hue University, Quang Tri Branch, Hue City 520000, Vietnam
 - ⁴ Faculty of Environment, Hanoi University of Natural Resources and Environment, No. 41A, Phu Dien Street, Hanoi 100000, Vietnam
 - ⁵ Institute of Environmental Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Hanoi 100000, Vietnam
 - ⁶ Institute of Research and Development, Duy Tan University, Da Nang 550000, Vietnam
 - ⁷ Faculty of Environmental Chemical Engineering, Duy Tan University, Da Nang 550000, Vietnam
- * Correspondence: cucphuong@hueuni.edu.vn (T.C.P.T.); nguyensexuancong4@duytan.edu.vn (X.C.N.)

Abstract: Elevated phosphorus (P) levels in water sources can result in eutrophication, which in turn causes environmental pollution and adversely affects aquatic ecosystems. Additionally, there is a risk of P depletion due to intensive exploitation and utilization. Therefore, the sustainable and efficient use of P, waste reduction, and P recovery from waste sources have become urgent priorities. This article aims to provide the most current assessments of the P regeneration process and its origins within waste and wastewater. This work also evaluates P recovery, as to its mechanisms, influencing factors, and performance. Moreover, the review presents comprehensive results from pilot and full-scale applications of P recovery. Further perspectives are analyzed, including economic feasibility, potential environmental impacts, research needs, and opportunities for improving P recovery.

Keywords: adsorption mechanism; biochar; phosphorus recovery; waste streams



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1. Introduction

Contemporary waste sources encompass a diverse range, spanning agricultural residues, food waste, sewage sludge, and industrial remnants. These waste materials contain valuable phosphorus (P) compounds, raising environmental concerns and offering untapped potential. A forecast study suggested that P fluxes from agriculture and domestic wastewater increased annually from 7.0 to 8.4 teragrams of P in 2010, with projections indicating a doubling by 2100 [1]. This underscores the critical significance of P treatment and recovery measures.

Research on P and biochar commenced in 2011 with just four studies. The year 2017 witnessed a significant increase, with 24 studies, and by 2022, the number had surged to 106. From 2021 to 2023, approximately 100 research projects were undertaken in this field (Figure 1a). These studies reveal clusters predominantly focused on adsorption properties, nutrients, and various chemical agents (aluminum, calcium, chlorine compounds, and iron). Other significant areas include eutrophication, isotherms, kinetics, and phosphorus recovery (Figure 1b). The “phosphorus recovery” and “recovery” themes are closely linked to adsorption, pyrolysis, phosphate, pollutants, and fertilizer. While phosphorus recovery was historically associated with sorption research, with many publications, it was not a concentrated area of independent research interest.

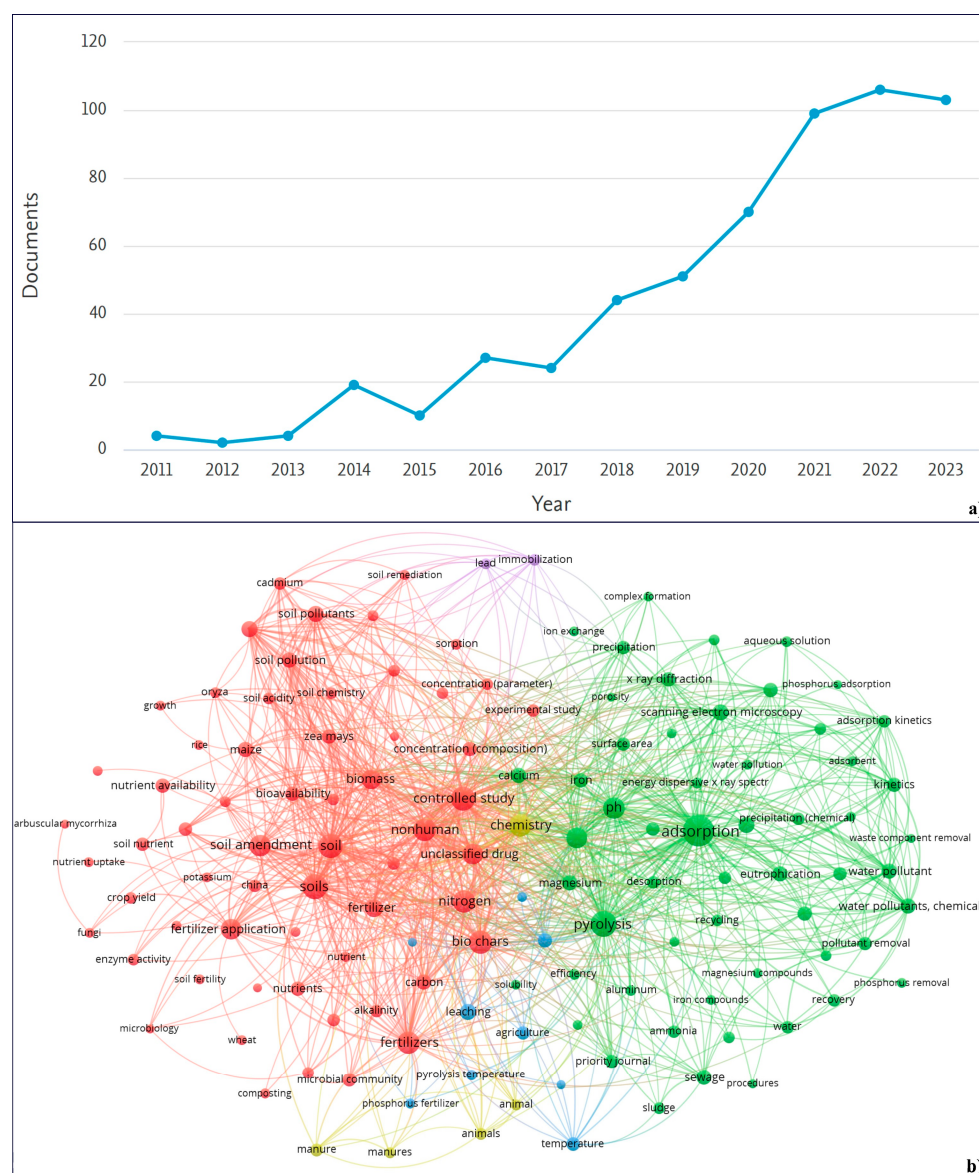


Figure 1. The number of research articles in the field of “phosphorus” and “biochar” (a) and co-occurrence networks of index keywords (b). A minimum keyword occurrence threshold of 20 was applied. The data was sourced from Scopus, and the visualizations were generated using the VOSviewer software version 1.6.19 (<https://www.vosviewer.com>, accessed on 10 June 2023).

Biochar forms when biomass undergoes thermal decomposition in oxygen-depleted conditions. It consists of two types: pristine biochar and activated biochar. Pristine biochar has a small surface area, ranging from 8 to 132 m²/g, or it can be even more significant, reaching up to 490.8 m²/g, with corresponding pore volumes of 0.016–0.083 cm³/g. On the other hand, activated biochar has a significantly larger surface area and pore volume, reaching up to 3263 m²/g and 1.772 cm³/g, respectively [2]. Biochar, distinguished by its expansive surface area, porous structure, and favorable chemical attributes, stands poised to function as a versatile adsorbent and immobilization medium for P treatment and recovery [3,4]. By redirecting P from waste streams and effecting its conversion into a reusable resource, the biochar-based recovery approach offers an innovative and sustainable solution, tackling waste management issues and P resource scarcity.

The raw materials used to produce biochar are highly diverse, as any form of organic matter can be subjected to thermal decomposition to create biochar. To improve waste management and support environmental conservation, agricultural byproducts such as rice

straw, corn stalks, peanut shells, rice husks, fruit peels, livestock manure, kitchen scraps, and sewage sludge are converted into biochar fuel through human intervention [5]. The elemental composition varies with different types of raw materials, resulting in differences in the physicochemical properties of the resulting biochar. Even with the same raw material, altering pyrolysis conditions such as temperature, residence time, and heating rate leads to variations in surface area, functional groups, and pore size [6,7]. Biochar produced from sesame straw, when the pyrolysis temperature was raised from 500 to 600 °C, exhibited an increase in effective area from 46.9 to 289.2 m²/g, and total pore volume increased from 0.0716 to 0.1433 cm³/g [7]. Researchers have noted alterations in the biochar's porosity and surface area during the pyrolysis of straw and lignosulfonate for biochar production. These measurements increase as the pyrolysis temperature rises from 200 to 400 or even 600 °C because higher temperatures increase feedstock decomposition, further breaking down the original structure. The straw biochar and lignosulfonate–straw produced at 200 and 400 °C contained alkyl carbons, but at 600 °C, these functional groups were not present. Conversely, the aromatic carbon content was higher in the 600 °C pyrolysis product but lower in the 200 °C pyrolysis product [8].

In agricultural production, organic waste materials can transform into biochar, reducing waste. Biochar becomes environmentally friendly, as it sequesters carbon in the soil, thereby reducing CO₂ emissions [9]. Also, combining biochar with fertilizers enhances their effectiveness, making it a viable solution for circular economy practices [10]. Moreover, biochar production helps to manage organic waste, recovers organic carbon, and provides macro- and micronutrients to the soil for agricultural purposes [11]. Therefore, biochar helps to reduce agricultural emissions from chemical fertilizers, as the demand decreases [12].

Utilizing Mg-biochar derived from diverse biomass sources like coffee husks and palm tree trunks has proved to efficiently capture NH₄⁺ and PO₄^{3−} from wastewater while also serving as a durable fertilizer [9]. Biochar also improves soil porosity and water retention, creating conditions favorable for plant growth [13]. Several studies have validated these results, such as a study on maize cultivation comparing inorganic P fertilization to biochar P fertilization. The findings indicated that applying biochar in conjunction with P fertilization led to enhanced plant growth, manifesting as a remarkable 30% boost in seed quantity and a notable 21% increase in seed weight compared to the sole use of P fertilization [14].

Balancing the management of water pollution caused by P with the growing demand for P-containing fertilizers in agricultural production poses significant challenges for sustainable development today. Many studies have shown that biochar has many favorable characteristics for P adsorption. Slow-release fertilizers (SRF), recognized for incorporating nutrients in forms of poor solubility [15], are crucial for extending crop utilization periods. Extensive research has been conducted seeking to enhance P utilization, reduce losses, and recover P from wastewater using the SRF technique [16]. However, biochars made from traditional feedstock materials such as agricultural byproducts like peanut shells [17], sugarcane bagasse [3], forest biomass such as *Mimosa pigra* [3], red oak, longleaf pine wood shavings, hard maple sawdust [18], and pine sawdust [17] often fail to adsorb large amounts of P. Among these materials, biochar from pine sawdust exhibited the highest sorption capacity, reaching 15.11 mg/g [17]. Biochar from the direct thermal processing of biomass feedstock often needs more essential nutrients to be used effectively as fertilizer. Therefore, this necessitates the supplementation of nutrients for its efficient utilization as fertilizer. Various methods exist for producing SRF, such as pyrolysis, impregnation, sealing, and granulation.

When subjected to modification, the resulting product exhibits significantly improved P-removal capabilities. Modified biochar (*Mimosa pigra*, AlCl₃ salt) shows a 14-fold increase in adsorption capacity (reaching 70.6 mg PO₄^{3−}/g) compared to unmodified biochar [4]. In a study on the P extraction of biochar from hard maple and red oak, modified biochar with MgO demonstrated an 11-fold increase in adsorption capacity (reaching 29.22 mg/g) compared to raw biochar [18]. Also, biochar with a new core–shell structure

(γ - $\text{Al}_2\text{O}_3/\text{Fe}_3\text{O}_4$ -biochar) derived from *C. korshinskii* exhibited a remarkable P adsorption capacity of 205.7 mg/g. Furthermore, this biochar type maintained an adsorption efficiency of 91%, even after five subsequent reuses [19].

Numerous studies have explored the treatment and recovery of P using biochar from various waste streams, focusing on sources, mechanisms, influencing factors, and efficacy to demonstrate and enhance biochar's potential for P removal and recovery. Several reviews focused on biochar P-related topics, such as the influence of biochar on the fate of P in soil and water [20], P utilization in soil through biochar incorporation [21], and nutrient treatment using biochar [22,23]. Yet, there is lacking a comprehensive study summarizing and delving into phosphorus recovery, covering its sources, mechanisms, performance, and future potential at various scales (mesocosm, pilot, and full-scale). This study aims to explore P regeneration in waste and wastewater, along with the treatment and recovery mechanisms, influencing factors, and performance of biochar. Moreover, it reviews results from pilot and full-scale P-recovery applications, assesses economic feasibility and potential environmental impacts, identifies research needs, and explores opportunities for improvement.

2. Source and Flow of Phosphorus in Waste Streams

2.1. Phosphorus in Wastewater

Wastewater containing high concentrations of P is an issue attracting attention due to its impact on the integrity of water ecosystems and the looming potential for a resource crisis concerning P. Without treatment or recovery of P in wastewater, residual P excess can enter water sources, causing eutrophication [24–26]. As industry and agriculture continue to advance, there is a noticeable rise in residual P content within the wastewater. This escalation can be attributed to several factors, including human sewage, livestock activities, agricultural runoff, and industrial discharges [27,28].

P enters the domestic wastewater stream through human metabolic products (feces, urine), food residues, and detergents [29]. Domestic wastewater usually contains orthophosphate (57–95%), in addition to P in other biological compounds, e.g., nucleic acids, phospholipids, and phosphorylated proteins [30–32]. The concentration of P in domestic wastewater is usually lower than that of industrial and livestock wastewater. Depending on the urban or rural area, the total phosphorus (TP) concentration in domestic wastewater can vary from 5 to 30 mg/L [25,31,33–35]. A previous study on the P load associated with domestic wastewater entering a municipal wastewater treatment system in the United Kingdom (UK) showed that daily human diets contribute 40% of the P in sewage. Furthermore, the P load from household laundry detergents is 0.12 g/person/day, accounting for 14% of the P generated from domestic wastewater. About 8.7% of the P was lost from automatic detergents to the sewer system, and this number is likely to increase because as society develops, automatic detergents are used more and more [26]. In addition, 1% of the P was contributed from personal care products. Overall, the individual contribution tends to increase because P is one of the main components of synthetic detergents. Total P contributed by human activities varied from approximately 0.1 to 4.8 g/person/day, averaging about 2.7 g/person/day [36].

Meanwhile, with the rapid development of livestock and agricultural production, much wastewater containing P is discharged into surface water. Studies show that 56% of total P emissions came from farm sources [37,38]. The primary P sources in agricultural and livestock wastewater are manure and fertilizers. In agriculture, fertilizers are compounds that provide nutrients indispensable for plants; the primary nutrients in fertilizers include N, P, and K. If applied in excess or improperly, part of the substance's nutrients, including P, will be lost from the soil and seep into groundwater sources, after entering wastewater streams. A global forecasting model that quantifies P levels in agricultural wastewater reveals that the annual growth rate ranged from 5.7 to 6.1 g/L in 2010 and is projected to double by 2100 [1]. In addition, livestock wastewater is also a significant P source, within which pig industry wastewater had a high P concentration, reaching 780 mg TP/L [39]. The

wastewater's TP concentration exhibited notable variation in poultry production, ranging from 15 to 446 mg/L [40]. Similarly, the TP concentration in the dairy industry ranged between 12 and 266 mg/L, with cow manure as the primary P source [41,42].

In industry, P originates from detergents, preservatives, and other H_3PO_4 products. Detergents containing P are found in chemical and cosmetic industries and can be used as surface cleaning agents in manufacturing plants and metal cleaning, and have the potential to cause P loss [43,44]. The food industry is one of the sources of P due to preservatives containing a significant amount of P [45–47]. P can also be lost when found in fertilizer production and many other industries [48,49]. Industrial sewage from animal and plant sources had high TP concentrations, ranging from 12 to 780 mg/L and 35 to 350 mg/L, respectively [25]. The lowest TP concentrations (0.3–2.3 mg/L) were observed in the aquaculture industry, since the wastewater volume of 10,000 m^3 /day plays a fundamental role in diluting P levels [25,50]. In addition, the cellulose and tanning industries had TP concentrations <1 mg/L [51,52]. The concentration of P in wastewater from several industry sectors is summarized in Table 1.

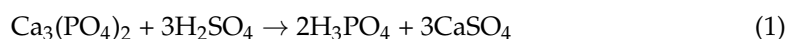
Table 1. P concentration in wastewater of different industries.

Type of Water	TP (mg/L)	PO_4^{3-} P (mg/L)	Refs.
Olive-oil mill	64–350	60–114	[53–55]
Winery	35–77	35	[56–58]
Food industry	153.6–328.4		[59]
Abattoir	28–49	23–40	[60,61]
Pulp and paper	0.5–24	0.01–23	[62,63]
Laundry	3.25–12	1.7–4	[64–66]
Tannery	0.4–21	0.06–7	[67–70]

2.2. Phosphorus in Waste

Every year, 18.9 million tons of P are produced, of which 75% are used as fertilizers and 25% are used for industrial and other purposes. However, the amount of P wasted is considerable: 18.5 million tons as solid waste and 1.32 million tons as emissions into the air and water [71]. Moreover, human waste is estimated to contribute around 5 million tons of P annually, encompassing feces, urine, and household cleaning products, while animal manure contributes between 20 and 30 million tons (2010) [72]. A contemporary challenge is the recovery of P from waste materials. Animal waste and activated sludge from wastewater treatment are significant P sources. A previous study has shown that the proportion of P lost in animal waste is extremely large (approximately 40%) [73]. Animal manure is an excellent source of organic matter and nutrients. The amount of P found in feces differed for each livestock industry, ranging from 3.2 to 25 kg/ton of waste, in which chicken manure was the most significant source [74].

P will gradually accumulate within activated sludge through biological or chemical wastewater treatment. About 1.3 million tons of P enter wastewater treatment plants yearly [75], where 90% of P is eventually retained in the sludge [76]. Depending on water quality and treatment conditions, P can account for 2–15% of the dry mass of the activated sludge in the form of polyphosphate, orthophosphate, and organic phosphate [77–79]. In addition, other sources of P-containing waste that need to be considered are the by-products generated in industrial production, including phosphogypsum and ore slag. Phosphogypsum is a by-product in the production of phosphoric acid from phosphate rock, according to the simple Equation (1):



The amount of phosphoric acid produced is not entirely recovered; a portion of the P remains within the plaster, referred to as Phosphogypsum. The total amount of P in the Phosphogypsum made each year was estimated at 0.3–2.2 Mt [72]. Phosphogypsum, in certain conditions, can be used to improve soil and reduce erosion; however, it is

noteworthy for its elevated pollutant content [80]. Another by-product containing P is the slag from the ore smelting process, which is characterized by a composition containing approximately 12% P_2O_5 . The P content in the ore slag is relatively high, rendering it a continuing choice for fertilizer use into modern times [72]. P-containing waste from biomass combustion and coal ash contributes significantly, ranging from 0.1 to 2 Mt for waste from biomass incineration and 1 to 10 Mt for waste from coal ash [72].

As such, a significant amount of phosphorus is wasted in solid waste, emissions, and wastewater, underscoring the urgent need for efficient phosphorus recovery. Exploring diverse sources containing phosphorus, from the waste of animals and humans to industrial by-products, opens potential pathways for sustainable phosphorus recovery, aligning with environmental conservation goals.

3. Phosphorus Recovery Mechanisms

Researchers have identified two main mechanisms of P adsorption onto biochar through various measurements: physical and chemical adsorption (Figure 2). P is also adsorbed onto biochar and processed through the biological corrosion mechanism [81]. In physical adsorption, phosphate ions (PO_4^{3-}) are attracted to the biochar's surface and pore spaces through electrostatic interactions [19,82–84] and pore filling [85]. The negatively charged phosphate ions are attracted to the positively charged chemical moieties on the carbonized exterior. Additionally, the pore spaces of biochar provide sites for the physical trapping of phosphate ions. Chemical adsorption involves ion exchange [86,87], precipitation [84,85], or complex formation [19]. Biochar can exchange ions with the surrounding environment, and in the case of P treatment, it can exchange phosphate ions with other ions in the solution. Precipitation occurs when certain conditions lead to the formation of insoluble P compounds on the biochar's outer layer. Complex shape refers to the origination of chemical complexes between P and functional groups on the biochar's surface [83,88]. These adsorption mechanisms do not exist independently but co-occur during adsorption.

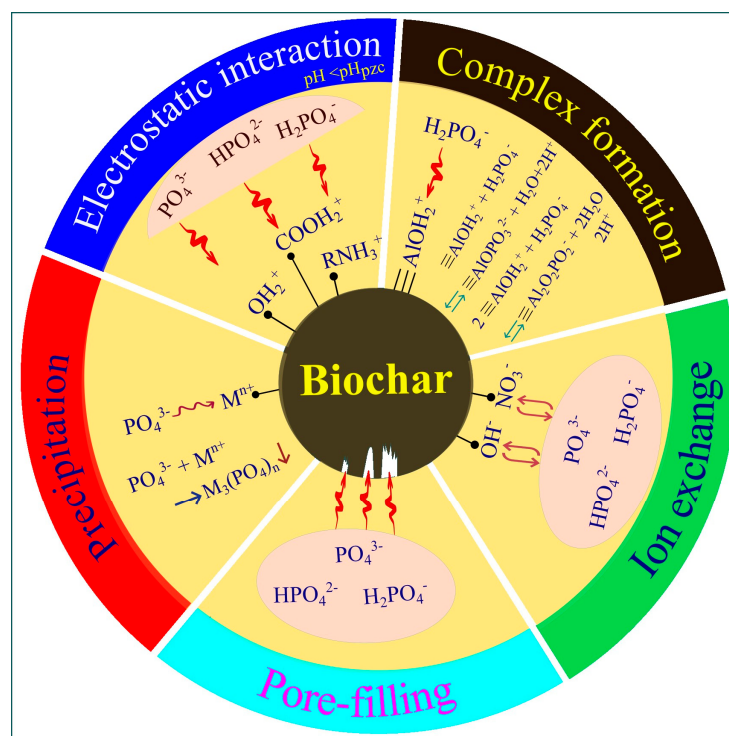


Figure 2. The main mechanisms of PO_4^{3-} adsorption onto biochar.

The specific surface charge of biochar, as determined by its point of zero charge, plays a significant role. When the pH of the solution is lower than the point of zero charge (pH_{pzc}), the functional groups on the biochar's surface become positively charged [4]. At the same time, the phosphate ions remain negatively charged. This electrostatic attraction between the oppositely charged ions is the dominant mechanism driving phosphate adsorption onto modified biochar. Electrostatic attraction is the dominant mechanism in PO_4^{3-} adsorption onto modified biochar [88,89].

Cationic ions, such as Ca^{2+} , Mg^{2+} , Fe^{3+} , and others, are commonly found within biochar. These ions can bond with anionic ions such as OH^- , and NO_3^- . When biochar is introduced into a solution containing PO_4^{3-} ions, an exchange of these anionic ions with the PO_4^{3-} ion can occur. As a result of electrostatic interaction and ion exchange, a chemical precipitation process in the form of phosphate precipitation [89,90] can take place. Utilizing the solubility product constants of the substances, we determined the equilibrium concentrations of the ions (Table 2). Precipitation will be favored for the ions with lower concentrations. Biochars containing Al^{3+} , Mg^{2+} , and Ca^{2+} ions tend to form phosphate precipitates rather than hydroxides. Therefore, the adsorption process via chemical precipitation is more likely to occur.

Table 2. Solubility and equilibrium ion concentrations of common substances in phosphate precipitation adsorption.

Substance	Solubility Product [91]	The Molarity of Cationic (M^{n+}) In the Saturated Solution	The Molarity of Anionic ($\text{PO}_4^{3-}/\text{OH}^-$) In Saturated Solution
AlPO_4	9.8×10^{-21}	9.9×10^{-11}	9.9×10^{-11}
$\text{Mg}_3(\text{PO}_4)_2$	1.0×10^{-24}	1.9×10^{-5}	1.2×10^{-5}
$\text{Ca}_3(\text{PO}_4)_2$	2.1×10^{-29}	2.2×10^{-6}	1.4×10^{-6}
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	9.9×10^{-16}	3.1×10^{-8}	3.1×10^{-8}
$\text{Al}(\text{OH})_3$	1.3×10^{-33}	2.6×10^{-9}	7.8×10^{-9}
$\text{Mg}(\text{OH})_2$	5.6×10^{-12}	1.1×10^{-4}	2.2×10^{-4}
$\text{Ca}(\text{OH})_2$	5.5×10^{-6}	1.1×10^{-2}	2.2×10^{-2}
$\text{Fe}(\text{OH})_3$	2.8×10^{-39}	1.0×10^{-10}	3.0×10^{-10}

The compounds of precipitates can be represented by the general formula M_mX_n . In the equilibrium state, there is an equilibrium relationship:



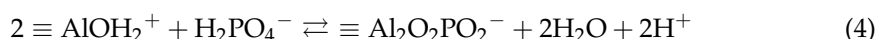
The solubility product constant (K_{sp}) is the equilibrium constant for a solid substance dissolving in water to produce a saturated solution [92].

The relationship between the concentrations of ions in the saturated state and the solubility product is expressed through this formula: $[\text{M}^{n+}]^m \cdot [\text{X}^{m-}]^n = K_{\text{sp}}$. Based on this, the solution's molarity of cations and anions can be calculated, as illustrated in Table 2.

Although they all can form phosphate precipitates, based on the calculations in Table 2, the molarities of cationic ions (M^{n+}) in saturated solutions follow the order $\text{Al}^{3+} < \text{Fe}^{3+} < \text{Ca}^{2+} < \text{Mg}^{2+}$. If we only consider the adsorption mechanism through chemical precipitation, biochar enriched with Al^{3+} ions, which has the lowest saturation concentration, shows the most favorable conditions for phosphate precipitation. However, as previously analyzed, the adsorption mechanism of PO_4^{3-} onto biochar involves multiple simultaneous mechanisms. In assessing P removal capabilities among biochars sourced from industrial tea waste, Al^{3+} -enriched biochar, and Fe^{3+} -enriched biochar, it was found that Mg^{2+} -enriched biochar exhibited a lower adsorption capacity [82]. The exchange of cations and precipitation to adsorb PO_4^{3-} could also occur when simultaneously treating NH_4^+ and PO_4^{3-} to form $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, known as struvite, when using Mg-biochar for the recovery of P and N [9]. The adsorption mechanism primarily involves electrostatic interactions through monolayer adsorption on the biochar's surface. Additionally, surface

precipitation and ligand exchange processes occur when investigating the adsorption of Mg-biochar derived from fowl bedding, porcine excrement, and sewage residue as to P from triple superphosphate [89]. Similar adsorption mechanisms, including electrostatic attraction and chemical adsorption, were observed when studying Mg-Al-biochar derived from straw for P removal from domestic sewage [93].

Alongside the above mechanisms, the formation of complexes is also commonly observed. The functional groups on the biochar's surface can form inner-sphere complexes with the PO_4^{3-} group by directly bonding to metal oxide sites on the char's surface or through oxygen atoms capable of complexation within functional groups such as hydroxyl, carboxyl, and phenolic [94,95]. Cui et al. determined that the adsorption of P onto core-shell- $\text{Al}_2\text{O}_3/\text{Fe}_3\text{O}_4$ biochar follows electrostatic attraction, ion exchange, and inner-sphere complexation [19]. Spectral images demonstrated the replacement of surface hydroxide ions on the biochar's surface with phosphate ions. The adsorption kinetics indicated that phosphate adsorption followed a pseudo-second-order model, suggesting that the primary adsorption process was chemical adsorption involving the complexation reactions described by Equations (3) and (4).



During adsorption via pore-filling mechanisms, the adsorption capacity of biochar is notably affected by both its surface area and its pore structure. A larger surface area and a porous structure with small and medium-sized pores enhance the favorable adsorption sites for the adsorption process [96,97]. When the pH of the solution is lower than that of the pH_{pzc} of the adsorbent material, it becomes positively charged. At the same time, phosphate ions carry a negative charge, facilitating the adsorption process [4,93].

Competitive adsorption occurs in co-occurring ions with the same charge as PO_4^{3-} . This phenomenon diminishes the phosphate adsorption capacity of biochar. When other anionic ions are available in the solution, competition for adsorption occurs based on electrostatic interactions, leading to a decrease in the adsorption capacity of PO_4^{3-} . The extent of reduction depends on the nature of the cationic elements. For ions derived from ingredients with low electronegativity, such as SO_4^{2-} , the reduction in adsorption capacity was minimal (1.7–7.4%). However, F^- , which has a strong electronegativity, interacted strongly with the surface of the adsorbent material, resulting in a reduction in the adsorption capacity of PO_4^{3-} by 15.9–18.5% [19].

In summary, P adsorption onto biochar involves two primary mechanisms: physical and chemical adsorption. The distinctive feature of biochar's surface charge, particularly at low pH, predominantly dictates electrostatic interactions, playing a central role in PO_4^{3-} adsorption. The simultaneous presence of multiple sorption mechanisms, including electrostatic attraction, pore-filling, ion exchange, chemical precipitation, and the formation of complexes, has been identified in this study. These findings provide profound insights into the diversity and complexity of the processes of phosphorus adsorption onto biochar.

4. Capacity and Performance of Phosphorus Recovery

The adsorption and P-recovery efficiency can vary depending on the materials used, the manufacturing and modification methods applied, and the specific characteristics of the P-recovery process. Table 3 provides data on the influence of the factors forming biochar on its adsorption capacity and P-recovery efficiency.

Table 3. Material characteristics and findings from the literature relevant to P-recovery (TP and PO_4^{3-}).

Biomass	Modifier	Modification Method	Surface Area (m^2/g)	Wastewater Type	Biochar Dosage (g/L)	Time (h)	Temperature ($^{\circ}\text{C}$)	pH	Capacity	Recovery (%)	Refs.
Marine macroalgae	Aluminum electrodes using NaCl as an electrolyte	Electro-modification	45.46	The solution was prepared from KH_2PO_4 and H_2O	1 g/L	48	20	7	31.28 (mg P/g)	NA	[98]
Marine brown algae	Aluminum electrode	Electro-modification and pyrolysis	280.69	The solution was prepared from KH_2PO_4 and H_2O	1 g/L	24	20	6	245.1 (mg PO_4^{3-} /g)	99.9	[99]
Brown marine macroalgae	Graphite electrode-based electric field and MgCl_2	Combined electrochemical modification	56.42	The solution was prepared from KH_2PO_4 and H_2O	1 g/L	48	20	NA	620.6 (mg PO_4^{3-} /g)	NA	[100]
C. Kosinski	Iron and aluminum electrodes	Electro-modification	233.29	The solution was prepared from NaH_2PO_4 and H_2O	1 g/L	12	25	5	205.7 (mg PO_4^{3-} /g)	91	[19]
Palm tree trunk	MgCl_2	Chemical modification	NA	Sewage sludge ash and food wastewater	Equivalent Mg (275.3 mM) in biochar	24	25	9.6	NA	92.2	[9]
Ground coffee bean	MgCl_2	Chemical modification	NA	Sewage sludge ash and food wastewater	Equivalent Mg (275.3 mM) in biochar	24	25	9.6	NA	79.5	[9]
Straw	$\text{Al}(\text{NO}_3)_3$ and $\text{Mg}(\text{NO}_3)_2$	Chemical modification	42.88	Domestic sewage	2.5 g/L	2	45	6	89.37 (mg P/g)	72	[93]
Corn stover	Sulfur powder, iron powder	Mechanical ball milling	NA	The solution was prepared from KH_2PO_4 and H_2O	2 g/L	6	25	6	25.0 (mg P/g)	84.4	[83]
Eggshell and corn stalk	-	Co-pyrolysis	NA	Piggery effluent	0.3 g/L	24	18	6.8	557.0 (mg P/g)	>80	[101]
Pinewood	FeCl_3	Chemical modification	385.00	Wastewater	1 g in column (H: 50 mm, D: 16 mm)	8.3	NA	NA	17.5 (mg P/g)	99.9	[102]
Corn stover	FeCl_3 and MgCl_2	Co-precipitation	51.46	Biogas slurry	1 g/L	12	25	5.48–6.77	6.784 (mg P/g)	81.8%	[103]
Industrial waste: Red mud and walnut shell		Co-pyrolysis	28.80	The solution was prepared from KH_2PO_4 and H_2O	6 g/L	24	25	5	15.48 (mg P/g)	99.74%	[104]
Crab shells	FeSO_4	One-pot dipping method	NA	The solution was prepared from KH_2PO_4 and H_2O	0.5 g/L	8	25	7	149.27 (mg P/g)	NA	[105]

NA: Not available.

Table 3 shows the diverse range of materials used in biochar production and modification methods. Metal-modified ions, such as aluminum, iron, and magnesium, were used frequently. The specific surface area, total pore volume, adsorption capacity, and recovery rate vary depending on the chosen material, the biochar production process, and the modification methods employed. Among these factors, biochar modification can be a crucial process for enhancing P removal and recovery. One significantly improved method for adsorbing PO_4^{3-} by biochar is electro-modification, which exhibited an adsorption capacity of up to 205.7 and 245.1 mg P/g. Alternatively, the combined electrochemical modification achieved a similar adsorption capacity of 620.6 mg PO_4^{3-} /g (equivalent to 202.5 mg P/g). The co-pyrolysis of eggshells and corn stalks achieved remarkable P sorption (557.0 mg P/g). This outcome stems from high-temperature co-pyrolysis, which transforms the primarily CaCO_3 -based eggshell into distributed nano-sized CaO on the biochar. Concurrently, the released CO_2 acts as a catalyst, expanding the biochar's surface pores. In contrast, other modification methods resulted in adsorption capacities of less than 100 mg P/g.

The ability to recover PO_4^{3-} varies significantly among different types of biochar. When selecting the appropriate biochar for the recovery process, various factors should be considered, such as the availability of local raw materials and the manufacturing method, to choose the most economically viable biochar for the recovery process.

5. Pilot and Full-Scale Applications of P Recovery

Biochar techniques for P recovery are mainly applied in the treatment of domestic wastewater, urban wastewater, industrial wastewater, livestock wastewater, stormwater runoff, and leachate. Biochar can be involved in several different stages of the wastewater treatment process, such as biological filter tanks and wetland systems (Figure 3).

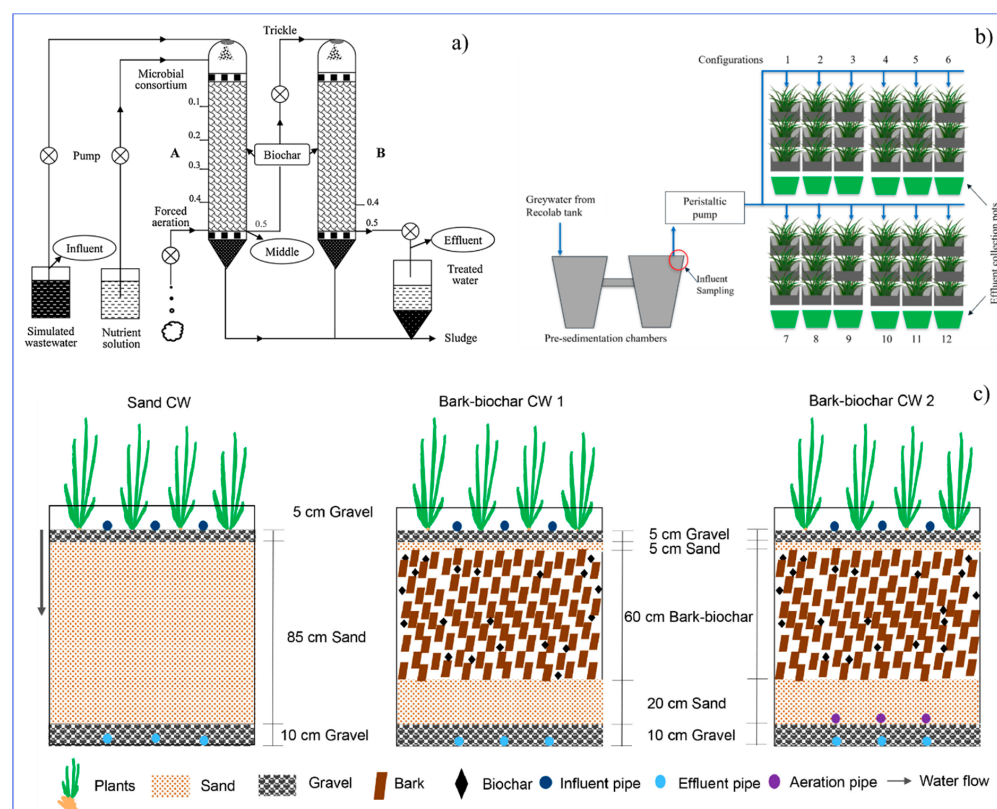


Figure 3. The diagram illustrates how biochar can be used for P recovery in biofilters (a) [106] and constructed wetlands (b,c) [107,108]. A and B in (a) denote aerobic (nitrification) and anaerobic (denitrification) conditions, respectively.

5.1. Integration of Biochar in Biological Filters

Biochar has been applied in pilot-scale biofilters for wastewater treatment, focusing on improving P-recovery efficiency (Table 4). Greywater treatment methods based on biochar-column filtration systems (BCFS) have gained popularity recently [109]. A pilot system repurposed greywater from a four-person household for irrigating nearby vegetables. With a 36 h retention duration, a multi-stage filtration device, including mulch, geotextile, charcoal, and gravel, removed 30.1% of TP [110]. Similarly, a filter system was implemented to treat household graywater from a family of seven in Musaffah, northeastern Jordan. This system, comprising a septic tank followed by an aerobic biochar filter, demonstrated efficient removal of $42 \pm 10.8\%$ of TP [111].

In Berlin, Germany, the Muenchehofe wastewater treatment plant conducted a ten-month pilot project to extract P from secondary wastewater, combining granular activated carbon deep layer filtration with coagulation. The project utilized two identical filter columns, each with a diameter of 0.15 m and a height of 4 m; one column utilized granular activated carbon (GAC) with quartz sand, while the other used GAC with gravel. Both configurations successfully removed P, reducing wastewater concentration to 0.1 mg/L [112]. In another innovative approach, a two-phase bio-trickling filter (BTF) system was implemented to address treatment of wastewater with elevated levels of nitrogen and P. This system incorporated sequential aerobic and anaerobic flow cell reactors, utilizing porous palm biochar as the packing material. Under optimal conditions (hydraulic retention time of 36–48 h, bicarbonate as the carbon source, and palm biochar packing), it achieved an 80% reduction in ammonium and a 68% reduction in total P [106].

A full-scale, three-stage filter was deployed to remove nitrogen and P from the effluent of anaerobic digesters in Madagascar. The system used locally available materials, including a submerged anaerobic filter containing bamboo chips for denitrification, a trickling filter made of coal granules, and a filter with scrap iron for P removal. Over 16 weeks, three parallel systems were used to treat around 70 L/day. The filters effectively removed P, chemical oxygen demand, and solids, with success rates of 31–50%, 67–75%, and 73–82%, respectively, as well as significantly transformed the nitrogen [113]. A study using bamboo biochar for improved nutrient removal in BAFs treating low C/N digested swine wastewater was implemented. The system achieved notable TP removal: 47.91% in Phase I and 53.12% in Phases II and III. Biochar in BAF encourages functional microorganism growth and enhanced microbial diversity, which are crucial for nitrogen and P removal in BAFs [114].

5.2. Integration of Biochar into Wetland Structures

Integrating biochar into wetland structures is one of the other promising methods for efficient P recovery (Table 4). Treating wastewater using constructed wetlands (CW) is a proven, effective technology that offers long-term solutions. Similarly, biochar provides inexpensive methods to clean wastewater and recover P with a low carbon footprint. Combining these two technologies can significantly increase a system's effectiveness [115].

The horizontal flow CW (HFCW) using biochar as media was applied in synthetic wastewater treatment. The integrated system achieved an average removal rate of 79.5% for TP and 67.7% PO_4^{3-} , surpassing the performance of wetlands using only gravel [115]. Three vertical flow CW (VFCW) columns filled with wood, corn cob biochar, and gravel have been explored as devices to recover P from anaerobically treated wastewater. It was demonstrated that the corn cob biochar VFCW column and the wood biochar VFCW column provided significantly higher treatment efficiencies for P (>71%) than did the gravel-VFCW. The enhanced pollutant removal ability of charcoal-added VFCWs was primarily due to increased adsorption capacity and microbial growth in the porous biochar media [116]. Another HFCW with electrolysis integration and biochar-modified material was investigated in a pilot-scale study. The investigation demonstrated significant enhancement of P removal (74.25%) by combining electrolysis and biochar substrate. This procedure used a sacrificial iron anode to generate ferric ions in situ, which increased P removal through

chemical-based deposition and physical adsorption mechanisms. Altered by ions from the iron anode, biochar proved effective in adsorbing nitrate and P, consequently enhancing effluent water quality [117].

An enriched hemp charcoal substrate was applied to HFCW cells for the pilot-scale residential wastewater treatment. During the 7-month study period, with a mean P injection of 15.5 mg/L (after primary treatment), the biochar-added HFCW continuously decreased $\text{PO}_4^{3-}\text{-P}$ concentrations in sewage to below 2 mg/L [118]. Saeed et al. investigated pilot-scale CW systems to treat raw sewage and recover P. The results showed that vertical flow CW that was filled with bamboo and wood biochar improved P removal, as follows: an inlet P concentration of 14.1 ± 8.2 mg/L (Phase I) and 7.0 ± 2.0 mg/L (Phase II) and an outlet P concentration of 6.1 ± 4.5 to 6.9 ± 5.5 mg/L (Phase I) and 6.5 ± 3.5 to 7.8 ± 2.1 mg/L (Phase II). Green walls in urban environments can be both an aesthetic feature and of practical use in greywater treatment [119]. Sami et al. evaluated the efficiency of treating actual greywater from a city district in a pilot-scale green wall with five different filter materials as substrates (biochar, pumice, hemp fiber, spent coffee grounds, and composted fiber soil). The biochar material showed promising TP treatment efficiency, with 57% [107].

Many studies detailing biochar application for P recovery are typically conducted at the pilot stage, with full-scale publications remaining relatively rare. This underscores the need for comprehensive insights into the effectiveness, on a full-scale level, of biochar application for P recovery. Strengthening research demonstrations at a full-scale level regarding the implementation of biochar for P recovery is imperative. However, full-scale implementation can also encounter challenges, including those relevant to capacity limitations, real-world conditions, long-term performance and sustainability, economic considerations, policy aspects, and regulations. Using biochar for P treatment must align with local regulations, including those governing waste management, nutrient management plans, and environmental protection. Therefore, full-scale research results will provide valuable information to designers, builders, researchers, and managers seeking to implement P recovery using biochar on a larger scale.

Table 4. Integrated biochar in pilot and full-scale wastewater systems for P recovery.

Wastewater Types	Country	Q (L/d)	Technology Types	Biochar Types	HRT (h)	Input PO ₄ ^{3−} -P (mg/L)	Output PO ₄ ^{3−} -P (mg/L)	Input TP (mg/L)	Output TP (mg/L)	Refs.
Greywater	Uganda	60	Filter system	Charcoal	36	NA	NA	24.1 ± 3.5	16 (30.1%)	[110]
Synthetic wastewater	Korea	10	CW	Woody biochar	72	16.3±1.1	5.3 ± 0.4 (67.7%)	36.1 ± 1.8	10.8 ± 1.1 (79.5%)	[115]
Greywater	Jordan	490	Filter system	Biochar	36	NA	NA	2.94–10.4	3.7 ± 1.4 (42 ± 10.8%)	[111]
Municipal wastewater	Germany	4.38	GAC and coagulation/filtration	Granular activated carbon	NA	NA	NA	0.54	0.1	[112]
Synthetic wastewater	China	NA	Bio-trickling filter (BTF)	Palm biochar	36–48	NA	NA	40–70	68%	[106]
Synthetic wastewater	China	30	Electrolysis-integrated CW	Bamboo biochar	24	0.5	0.17 (65.98%) (I) and 0.02 (96.73%) (II)	NA	NA	[117]
Domestic wastewater	Australia	NA	CW	Enriched hemp biochar	111.4	7.07–29.87	<2 (94.3%)	NA	NA	[118]
Municipal wastewater	Bangladesh	NA	CW	Bamboo and wood biochar	NA	NA	NA	14.1 ± 8.2 (I) and 12.7 ± 2.0 (II)	6.1 ± 4.5–6.9 ± 5.5 (I) and 6.5 ± 3.5–7.8 ± 2.1 (II)	[119]
Low C/N digested swine wastewater	China	NA	Bioreactor	Bamboo biochar	NA	NA	NA	20–35	14.98 (47.91%) (I) and 53.12% (II, III)	[114]
Greywater	Sweden	18	Greenwell	Biochar	NA	NA	NA	1.5	0.5 57 (%)	[107]
Anaerobic digester wastewater	Madagascar	71.3 (I) and 35.6 (II)	Trickling filter	Commercial biochar	NA	NA	NA	224 ± 51 (I) and 231 ± 17 (II)	139 ± 59 (I) and 202 ± 33 (II)	[113]

I, II, and III: Phases.

6. Future Perspectives

6.1. The Economic Feasibility of Biochar-Based P Recovery

P is scarce, which makes it a desirable product, but in reality, P is released excessively into freshwater, which can cause eutrophication and deterioration of water quality. Focusing on P recovery from point sources, particularly in wastewater treatment systems, is necessary, since recovering P from diffuse sources is expensive [120]. There are numerous ways to remove and recover P. However, in the future, investors will be drawn to low-cost, non-toxic, energy-efficient methods that have excellent processing efficiency and are simple to use. An approach that fulfils the criteria above is wastewater treatment integrating biochar for resource recovery [121]. From an economic point of view, biochar application systems for P recovery should be designed for maximum P recovery in wastewater, along with low material, installation, operation, and maintenance costs [122].

A significant determinant of the economic viability of P recovery is the cost of producing biochar. This is based on several factors, including the choice of feedstock, the manner of production, the size of the business, and the amount of energy needed. Efficiently utilizing affordable raw materials and optimizing production processes can significantly reduce production costs. In the pilot scale plant, one tonne of biochar could be made for USD 710, utilizing microalgae as the feedstock [123]. Using maize stalk and potassium dihydrogen phosphate (KH_2PO_4), one tonne of P-rich biochar costs around USD 3050/ton [124].

Biochar production often yields valuable byproducts such as heat or syngas. Leveraging these byproducts for energy generation or other value-added processes can enhance the economic feasibility of biochar-based P recovery. Utilizing these byproducts can offset production costs and provide additional revenue streams, thus improving the overall economic outlook. In addition to biochar, other pyrolysis products, such as bio-oil, are also produced; bio-oil can be sold for USD 410/ton and thereby contribute to reducing biochar costs [123].

A plethora of studies have indicated that biochar can be reused several times while maintaining its effective P sorption capabilities. Ai et al. demonstrated that biochar derived from corn stalks and CaO and prepared using ball milling held efficient P removal even after five regeneration cycles. The initial capacity of biochar was 91.54 mg P/g, and after multiple regeneration and reuse cycles, it remained at 75.03 mg P/g at the fifth cycle [125]. Akindolie et al. synthesized biochar by co-precipitating iron and lanthanum on biochar derived from coffee husks. They found efficiencies ranging from 71.5% to 97.8% in the initial cycles for P elimination. After five consecutive sorption cycles, the biochar maintained a treatment capacity of approximately 60% [126]. Moreover, Kizito et al. reported that the adsorbed PO_4^{3-} could be effectively desorbed from the spent biochar in neutral solutions (57–78%) and acidic solutions (75–88%). Regenerated biochar could re-adsorb up to 5.62 mg/g at the highest initial PO_4^{3-} concentration of 150 mg/L [127]. Alsawy et al. demonstrated that the operational cost of the wastewater treatment system significantly decreased when biochar was reactivated (regenerated) following the adsorption process, allowing it to be used for multiple cycles [128].

As a result, the production cost of biochar can be reduced not only by using readily available raw materials and obtaining by-products during the biochar production process but also by harnessing its practical reusability. This contributes to improving both economic and environmental sustainability.

6.2. Potential Environmental Impacts of Using Biochar for P Recovery

P is a major contributor to eutrophication in water bodies, leading to harmful algal blooms and degraded aquatic ecosystems. Biochar-based P recovery in wastewater treatment can potentially reduce P discharge into receiving water bodies, thereby mitigating nutrient runoff and improving water quality [111]. Biochar is an excellent example of one of the many circular-economy and zero-waste concepts that might be used to encourage economic actors to achieve carbon balance neutrality [112]. After the elimination process in

wastewater, biochar can be desorbed and reused to treat wastewater, which helps reduce the quantity of solid waste that needs to be dealt with. Following the P adsorption process in wastewater, biochar can be utilized as fertilizer to increase soil fertility. P adsorbed on biochar can be recycled and used again, which can lessen the demand for chemical fertilizers and avoid the overuse of P in agriculture, which can cause back-water pollution. Biochar incorporation improves the fertility and nutrient-holding capacity of soil. As a result, less land will need to be cleared for agriculture; less deforestation will occur, crop yields will rise, nutrient leaching will be decreased, and this will help to preserve natural ecosystems. Owing to its stable carbon structure, biochar has the potential to reduce atmospheric CO₂ levels, mitigating the total greenhouse gas emissions by 2.56×10^9 t CO₂ equivalent annually. This accounts for 5.0% of global greenhouse gas emissions, making it a valuable tool in moderating climate change. As per Kurniawan et al., the incorporation of biochar into soil can enhance agricultural health and yields while reducing CO₂ emissions by approximately one-eighth [129]. Biochar can act as a long-term CO₂ sequestration sink, effectively limiting the release of carbon back into the atmosphere.

6.3. Research Needs for Improving Biochar-Based P-Recovery Processes

Biochar-based P-recovery processes have shown great promise in addressing P scarcity and environmental problems. However, there are still some unresolved problems related to the biochar–wastewater P-recovery process:

(1) Anaerobic digestion (AD) is a crucial technique for the treatment of wastewater or wastes rich in organic matter [130,131]. AD of organic waste is a common technique for bioenergy production. Various enhancement tactics have been investigated recently seeking to increase the efficiency of AD processes [132]. A possible method to improve the AD process is using carbon-rich materials like biochar and activated carbon [133], without changing the infrastructure. Biochar can be added to anaerobic digesters to improve AD stability, enhance methane production, and adsorb contaminants (heavy metals, ammonia, and volatile fatty acids) in the waste [134–136]. The effectiveness of biochar's P recovery has been the subject of numerous investigations. However, no studies have reported on the efficiency of N P co-treatment and the ability to enhance methane production in AD tanks. Therefore, the resolution of this information will guide the widespread application of biochar in anaerobic digesters for P and N recovery and methane production.

(2) Emerging pollutants are a substantial concern and present difficult hurdles for P recovery. Emerging pollutants include pharmaceuticals, cosmetics, phenol derivatives, transformation by-products, and microplastics. In recent years, microplastics have also been found in various sources, including sewage sludge, organic waste, and wastewater. Because of their hydrophobic nature, microplastics can readily absorb toxic substances in waste streams, which challenges P recovery. Nonetheless, several studies have shown that biochar can efficiently adsorb emerging impurities from aquatic systems [137]. Most of these studies focused on biochar's adsorption and desorption capabilities for specific pollutants in natural wastewater [138]. As a result, a question arises about whether biochar's efficiency in P recovery is affected when dealing with water containing emerging contaminants.

(3) The interaction between biochar and microorganisms present in wastewater is another area of interest. Microorganisms are readily available in wastewater sources and are capable of self-cleaning when contaminant concentrations are low. The combination of biochar and microbial complexes can enhance the effectiveness of pollutant reduction [139]. Further studies on the interaction between biochar and microbial communities in waste should be carried out in order to advance the recovery of P from the laboratory scale to the pilot scale, e.g., by combining biochar with activated sludge aerobic systems, SBR, and other methods.

7. Conclusions

In the context of the rapid industrial and agricultural growth which has led to increased water pollution from P in recent years, remediation measures become crucial. P

sorption on biochar involves electrostatic interaction, complexation, ion exchange, pore filling, and precipitation. Among these methods, electrically driven biochar modification is the superior approach for enhancing adsorption. The results of P recovery in laboratory experiments demonstrated recovery levels of 72 to 99.9%. The potential of biochar for P remediation, from pilot-scale to practical applications, were also explored. CW and biofilters using biochar have demonstrated P-recovery efficiency levels ranging from 30 to 97%. While biochar's P adsorption capacity is acknowledged, its interaction with anaerobic digestion and emerging pollutants such as pharmaceuticals warrants further exploration. Understanding the interplay between biochar and microorganisms is essential for successful integration. A comprehensive investigation is also needed to facilitate practical, real-world applications.

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