



Removal of ammonium and phosphates from aqueous solutions by biochar produced from agricultural waste

F. Pantoja¹ · H. Sukmana¹ · S. Beszédes² · Z. László²

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Abstract

The concern about protecting water quantity and quality is one of the most severe challenges of the twenty-first century since the demand for water resources grows as the population and its needs grow. Additionally, and as expected, most human activities produce wastewater containing undesirable contaminants. On the other hand, the generation of agricultural waste and its inappropriate disposal causes further problems. Current wastewater treatment methods involve a combination of physical and chemical processes, technologies, and operations to remove pollutants from effluents; adsorption is an excellent example of an effective method for wastewater treatment, and biochar is currently one of the most valuable adsorbents. This review focuses on new research about applying biochar produced from agricultural waste as a low-cost and environmentally friendly method for removing ammonium and phosphates from aqueous solutions.

Keywords Biochar · Adsorption · Ammonium removal · Phosphate removal · Wastewater treatment

Introduction

Biochar is a carbonaceous material recognized as an important environmental management tool [1]. Today, caring for the environment and natural resources is an imperative mission because humanity is facing increasingly complex environmental challenges. On one hand, one of the challenges is maintaining water of sufficient quantity and quality to supply the population's necessities; on the other hand, agricultural activity has been intensively developed due to the need to produce food for the population. However, agricultural activity generates vast amounts of waste, which must be appropriately disposed of, and it is also necessary to search for new ways to add value [2]. Accordingly, in recent years research has focused on developing novel water treatment methods in which agricultural waste intervenes as an adsorbent material for water-pollutant compounds [3].

Water quality is crucial for public health, as used for drinking, domestic use, food production, or recreational

purposes. With population growth, increased amounts of nitrogen (N; ammonium and nitrate) and phosphorus (P; phosphate) are discharged in domestic sewage, and these are components that cause water eutrophication; additionally, agricultural activity and applying fertilizers and pesticides intensify the release of N and P [4]. Achieving economic growth and reducing poverty can be facilitated by ensuring a consistent and high-quality supply of water and sanitation, along with effective management of water resources [5]. The primary objective of the current research is to develop materials, processes, and technologies that enable the decontamination, management, and reuse of water. A prime illustration of this is the utilization of nitrogen and/or phosphorus that is obtained during the water decontamination process to produce fertilizers. This application exemplifies the global concept of circular economy, which the European Union defines as a 'system that maximizes the value of products by minimizing waste and keeping materials in use for as long as possible' [6].

Biochar is 'the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical properties suitable for safe and long-term storage of carbon in the environment' [7]. By the definition, biochar is considered to be a precursor to activated carbon. Although the feedstock material and production processes used to make biochar

✉ Z. László
zsizsu@mk.u-szeged.hu

¹ Doctoral School of Environmental Sciences, University of Szeged, Szeged, Hungary

² Department of Biosystems Engineering, University of Szeged, Szeged 6725, Hungary

and activated carbon are similar, biochar is produced at a lower temperature, resulting in more functional groups [8]. This situation also means that the price of biochar is lower than that of commercial activated carbon. Biochar can be produced from a wide range of raw materials and is currently used in environmental management practices such as soil improvement, waste management, energy production, climate change mitigation, and waste water treatment [1].

Several studies have demonstrated that the primary process involved in N and P adsorption on biochar is a practical, low-cost, and environmentally friendly option for recovery of nutrients from wastewater. The present review focuses on recent studies about the application of biochar produced from agricultural waste to remove ammonium and phosphates from aqueous solutions.

The study of biochar has gained great interest in the scientific community in the last decade; proof of this is the growing number of publications referring to biochar as an adsorbent in general and biochar as an ammonium and phosphate adsorbent specifically.

In the last decade, the number of publications referring to the use of biochar as an adsorbent material for compounds such as ammonium and phosphorus in SCOPUS has grown (Fig. 1).

Materials and methods

Biochar feedstock types, production technologies characteristics, and nutrient adsorption mechanism.

Feedstock types for making biochar

A wide variety of organic materials or biomass with a high carbon content can be used to yield biochar [9], including woody [10], herbaceous, and agricultural biomass [11–13]. To achieve the goal of circular economy and minimize environmental emissions, it is crucial to take into account various factors when selecting feedstock, including abundance, storage capacity, transportation costs, and the need for chemical treatment in cases where pre-treatment is required [14].

Biochar production technologies

The feedstock type has a significant impact on the textural features of biochar in terms of surface area, pore size, and pore volume distribution [15]. However, depending on the biochar fabrication technique, the new scorched organic matter can have different chemical and physical characteristics [16]. Biochar can be produced by slow/fast pyrolysis, gasification, flash carbonization, torrefaction, and hydrothermal carbonization [17].

Pyrolysis is carried out under oxygen-free conditions during the conversion process; nevertheless, pyrolysis ability may be distinguished by the pyrolyzed material's response time and the heating method [16]: using slow pyrolysis it is possible to achieve a 35% biochar yield [17], while a 26% biochar yield is achieved through fast pyrolysis [16].

Gasification is a thermochemical process through which organic matter is decomposed to hydrogen, carbon monoxide, and carbon dioxide principally; with this technology, a syngas yield of 85% is reached [17]. The gasification process

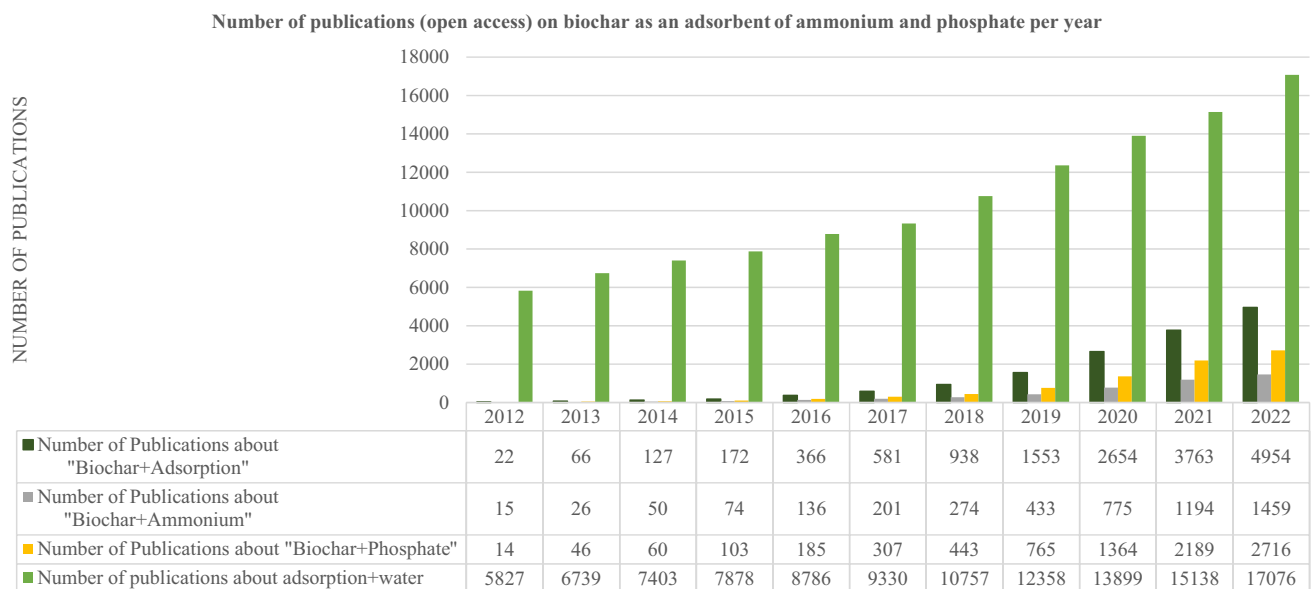


Fig. 1 Number of publications on biochar as adsorbent (accessed on 15 Dec 2022)

is intended to produce gaseous energy products. The product of biomass gasification is known as syngas; in this process, small amounts of char, ash, and tar are also produced [18].

During *flash carbonization*, biomass is placed in a vessel with an initial pressure in the range of 1–2 MPa and a flash fire is periodically lit at the bottom of the biomass. The carbonization time decreases with increasing pressure; in consequence, the volatile matter in the feedstock is converted into gaseous fuel, and the remaining fixed carbon is derived into biochar [19]. Using flash carbonization, it is possible to reach a biochar yield of 50% [20].

Hydrothermal carbonization is a wet pyrolysis that is carried out in a reactor with automatic electric heating [21]. With this technology, a hydrochar yield of 72% can be achieved [20]. Last but not least, pyrolysis-like torrefaction is a thermochemical process carried out at low temperatures and heating rates [22]; a biochar yield of 77% can be achieved through this process [20].

Types of biochar production technologies are summarized in Table 1. Besides the different types of technology used to produce biochar, it points out the characteristics, advantages, and challenges that must be taken into account when applying the technologies.

Modified biochar for water treatment

The modification of biochar is being sought to improve its characteristics for removal of impurities. Metal oxide and metal salt modification, acid–base modification, composite production, and ball milling modification are all typical ways of improving biochar's adsorption capability [33].

Metal oxide and metal salt modification The modified biochar has strong anion exchange capacity, precipitation, and electrostatic attraction, which increases its adsorption capacity: Inorganic phosphorus adsorption capacity is 1.46 times higher than that of unmodified biochar [34]. The metals used for this modification include magnesium, iron, aluminium, and manganese [35].

Acid–base modification The aims of acid modification are to eliminate impurities on one hand, and on the other hand to introduce acid functional groups on the surface of the biochar. Hydrochloric acid, sulphuric acid, nitric acid, phosphoric acid, oxalic acid, and citric acid are the acids used in this type of modification. With respect to alkaline modification, this has the objective of increasing the functional groups that contain oxygen. The most commonly used alkaline agents include potassium hydroxide and sodium hydroxide [35]. Moreover, the specific surface area of acid- and alkali-modified biochar can be raised by 10 and 14 times, respectively [33].

Composite production Biochar is impregnated with clay minerals such as kaolinite, montmorillonite, or bentonite, which alter the composition and physical characteristics of

the biochar, resulting in increased oxyanion sorption capacity [36]. Modifying biochar with clay minerals enhances its interfacial compatibility with pollutants, thereby boosting its adsorption capacity. For instance, the incorporation of montmorillonite in biochar increases the adsorption of ammonia approximately five fold [33]. Clay mineral–biochar composite has been demonstrated to have an efficient ability to co-adsorb ammonium and phosphate by electrostatic interaction and ionic bonding [37].

Ball milling modification Ball milling mechanically reduces the particle size to ultrafine or nanoscale sizes [38]. Compared to their non-ground counterparts, carbon-based materials treated by ball milling have a higher adsorption capacity, more oxygenated functional groups, and enhanced efficiency in environmental applications. The powder charge is subjected to the kinetic energy produced by the motion of moving balls, which causes the chemical bonds between the molecules involved to break and the particle size to decrease. The breaking of the materials' lattice structure results from a number of progressions including the transfer of mass and energy and the development of mechanical stress as a result of milling [38, 39]. With ball milling modification, the specific surface area increases in a range from 3 to 25–194 m²/g, depending upon the milling method used [40], considering the comparison between the pristine biochar and ball milled biochar [41].

Characteristics of biochar

The main characteristics of biochar are: the surface area, carbon content, stable structure, porosity, and cation exchange capacity. Thanks to the high surface charge density, biochar retains cations through the ion exchange process; moreover, a large surface area, internal porosity, and polar and non-polar surface sites allow biochar to adsorb nutrients [42]. It is worth noting that physical adsorption is determined by the structure and surface area of biochar, whereas chemical adsorption is determined by the biochar composition and type and quantity of functional groups [4].

Biochar generally has an alkaline pH; under different pyrolysis temperatures, the pH normally increases as the temperature rises due to the decomposition of acidic functional groups and the volatilization of organic acids [43]. Ammonium retention by biochar is due to electrostatic adsorption to surface functional groups containing negatively charged oxygen [42, 44]. However, the magnesium and calcium content of biochar gives it a high capacity to adsorb phosphate [8].

Biochar surface area and porosity (principally mesopores and part of macropores) are regularly measured using gas adsorption in water treatment and soil remediation. The European Biochar Certificate (EBC) and International Biochar Initiative (IBI) recommend the

Table 1 Types of biochar production technologies

Technology type	Temperature range (°C)	Residence time	Advantages	Desired product	Technological challenges	References
Pyrolysis	300–850	1–3 h	Easy operation, robust, and cost-effective; suitable for biochar production on a small scale	Biochar	<ul style="list-style-type: none"> Reaching and preserving high heat rates and reaction temperatures In accelerated pyrolysis systems, char removal and liquids recovery might be difficult During pyrolysis, gas conversion, the emission of chlorine from feedstock with a high Cl concentration may cause corrosion of the reactor containment and the development of deposits 	[16, 23–26]
Gasification	> 850	10–20 s	Gasification has lower biochar yield than pyrolysis, although biochar includes a lot of alkali salts, elimination of the drying step	Syngas	<ul style="list-style-type: none"> Repolymerization causes the production of soot On fine particles, tars dehydrate in the gas phase and interact with other pollutants Aerosol formation On colder surfaces, heavier tar components condense Clogging of fuel lines/injectors and clogging of particulate filters in internal combustion engines Tars induce rusting 	[16, 23, 26, 27]
Hydrothermal carbonization	180–300	1–16 h	More appropriate for feedstocks with a high humidity content, elimination of the drying step, hydrochar has higher atomic ratios of oxygen to carbon and hydrogen to carbon, rapid breakdown of hemicellulose, inexpensive and environmentally friendly method	Hydrochar	<ul style="list-style-type: none"> The elasticity limit of the materials introduced into the pressure tank must not be exceeded during operation Generation of safety problems in the case of feeding the continuous system against pressure It's possible that a heat recovery system from the hot process water, as well as post-treatment facilities for the char, will be required 	[16, 23–26]
Flash carbonization	300–600	≤ 30 min	Quick/fast process with high efficiency	Biochar	<ul style="list-style-type: none"> Under particular process settings with specific feedstocks, rapid pressure increases in the carbonization container can be obtained/experienced at ignition The elasticity limit of the materials introduced into the pressure tank must not be exceeded during operation 	[16, 28, 29]

Table 1 (continued)

Technology type	Temperature range (°C)	Residence time	Advantages	Desired product	Technological challenges	References
Torrefaction	200–300	10–40 min	Increase in biomass energy density, fuel with uniform quality, mainly as a result of devolatilization mechanism, better grindability, higher hydrophobicity and suitable to wet biomass, better yield of biochar, resistance to microbial decomposition	Biochar Bio-oil	<ul style="list-style-type: none"> • Because of the safety concerns of producers, self-heating is a major problem when using solid fuels like coal, biomass, and biochar • During torrefaction at temperatures between 200 and 350 °C, persistent organic pollutants can produce • Because the torrefaction process rises the ash concentration of end products, combustion and gasification of torrefied biomass are limited • The problem of tar, emission of greenhouse gas and volatile matter is also something that has to be handled, especially in industrial scenarios 	[24, 26, 30–32]

Brunauer–Emmett–Teller (BET) process to analyse the nitrogen adsorption isotherm to determine the surface area [45].

Biochar's porous structure is advantageous for sorption because it can accommodate different pore sizes required for variable accessibility induced by distinct kinetic diameters of the adsorbate. This allows for effective pore filling in the sorption process. In conclusion, the surface area and porosity of biochar are critical in controlling the rate and kinetics of chemical reactions, as well as the pH [45].

Dehydroxylation, dehydrogenation, and aromatization of feedstock during pyrolysis produce surface functional groups that can be basic or acidic and play an important role in P or N adsorption. Acidic functional groups with a negative charge attract cationic ammonium species and exchange H⁺ on the surface of biochar, while basic surface functional groups with a positive charge contain OH ions and exchange phosphate ions in an aqueous solution [46]. An important research affirmation suggested that biochar produced in low temperature pyrolysis contains more functional groups [47].

Table 2 presents the principal characteristics of biochar obtained from waste, showing some examples of the principal characteristics of biochar from different feedstocks, conditions of temperature, residence time, and the technology chosen for elaboration of the biochar, as well as characteristics of the biochar such as the BET surface area, micropore volume, and the type of functional groups.

Generally, a higher carbonization temperature results in a higher specific surface area, e.g., hydrothermal carbonization of rice husk at 180 °C produced a variety of functional groups and BET area of 5.02 m²/g [48], but carbonization of sugarcane bagasse at 700 °C created biochar with more functional groups and a greater BET surface area (131 m²/g) [49]. The pyrolysis process has a critical temperature, beyond which subjecting the biomass to higher temperatures accelerates the release of volatile compounds, resulting in the development of a porous structure and an increased specific surface area [53]. Generally, feedstocks producing aromatic functional groups during pyrolysis, e.g., sugar cane bagasse, soybean stover, and oak sawdust, are advantageous for ammonium removal [49, 51, 52], while feedstocks producing mainly oxygen-containing functional groups e.g., rice husk and wheat straw, have demonstrated good results in terms of phosphate elimination. Overall, it is evident that the preparatory conditions and type of feedstock used to produce biochar determine its characteristics and applicability.

Methods for characterizing biochar

The characterization of biochar is conducted with three main objectives in mind: (1) to get a better understanding of biochar's physical and chemical characteristics, as well as changes in biochar features as a result of manufacture,

Table 2 Principal characteristics of biochar from waste

Biochar feedstock	Conditions of manufacturing biochar	Residence time (min)	BET surface area (m ² /g)	Micro pore volume (cm ³ /g)	Functional groups	Aqueous solution conditions	Kinetic and adsorption capacity	References
Rice husk	Hydrothermal carbonization 180 °C Pressure: 70 bar Pyrolysis 700 °C	20 60	5.02 131	0.025 not mentioned	–OH Si–O–Si C–O C–O–C Methyl C–H Aromatic carbonyl/ carboxyl C=O Aromatic C=C Aliphatic C–O–C Alcohol –OH Aromatic C–H	Synthetic solution with 20 mg/L of ammonium as initial concentration Synthetic phosphate solution with range of initial concentration 25–400 mg/L	Adsorption capacity: 0.89 ± 0.4 mg/g NH ₄ ⁺ kinetic and isotherms models not mentioned Adsorption capacity: 13.21 mg/g PO ₄ ^{3–} Langmuir isotherm Kinetic model not mentioned	[48] [49]
Wheat straw	Pyrolysis 550 °C	120	55.24	Not mentioned	Oxygen-containing functional groups	Synthetic solution with 40 mg/L of ammonium as initial concentration	Adsorption capacity 2.08 mg/g NH ₄ ⁺ was obtained with Langmuir isotherm. Pseudo-second-order	[50]
Soybean stover	Pyrolysis 700 °C	180	420.33	0.11	O–H Aromatic =C–H Aromatic =C–H	Synthetic phosphate solution with range of initial concentration from 10 to 200 mg/L	Langmuir and Freundlich isotherm. Pseudo-second-order	[51]
Oak sawdust	Pyrolysis 300 °C	30	Not mentioned	Not mentioned	Phenolic =OH and carboxyl C=O	Synthetic ammonia solution with initial concentration of 25.7 mg/L. Synthetic phosphate solution with initial concentration of 61.3 mg/L	Adsorption capacity 11.2 mg/g ammonium and 4.5 mg/g phosphate Langmuir isotherm. First-order model	[52]

circumstances, and feedstocks; (2) to assess the potential applications of biochar in various fields; and (3) to study biochar contaminants and ecotoxicological parameters [54].

Figure 2 shows a summary of methods for analysing the chemical and physical characteristics of biochar. Biochar can be characterized by its chemical properties, physical properties, surface morphology, and thermal stability. Chemical characterization involves pH measurements, electrical conductivity, and cation exchange capacity. Physical properties, such as surface area and pore size, can be determined by means of adsorption methods (BET isotherm measurements), while particle size distribution can be determined by particle size analysers. Porosity, bulk density, and solid density can be measured by means of mercury porosimetry. Surface morphology can be followed by scanning electron microscopy (SEM), while distribution of surface elements can be determined by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDX). Surface functional groups are measured by Fourier-transform infrared spectroscopy (FT-IR); surface chemical compounds can be determined by X-ray photoelectron spectroscopy (XPS). Thermal stability can be followed by thermal gravimetric analysis, while determination of chemical composition can be fulfilled by X-ray fluorescence spectroscopy. Raman spectroscopy can be used for determination of aromaticity [54].

Adsorption kinetics and isotherm models

Regarding kinetic models, Table 3 summarizes the equations and parameters of kinetic models and their respective units and parameter description.

Equations and parameters of isotherm models are summarized in Table 4; these models were used for decades to describe the interactions between adsorbates and adsorbents at equilibrium. Several research studies estimated the value of the maximum adsorption capacity using the Langmuir model [48].

The Langmuir isotherm assumes that the adsorbate forms a monolayer on a homogeneous adsorbent surface, whereas the Langmuir kinetic model is used to describe adsorption equilibrium data [56].

Results and discussion

Results for removal of ammonium and phosphates from aqueous solution using modified biochar originated from agricultural waste in recent research

The primary objective of utilizing biochar in the adsorption process is to eliminate nitrogen and phosphate from

Fig. 2 Biochar characterization

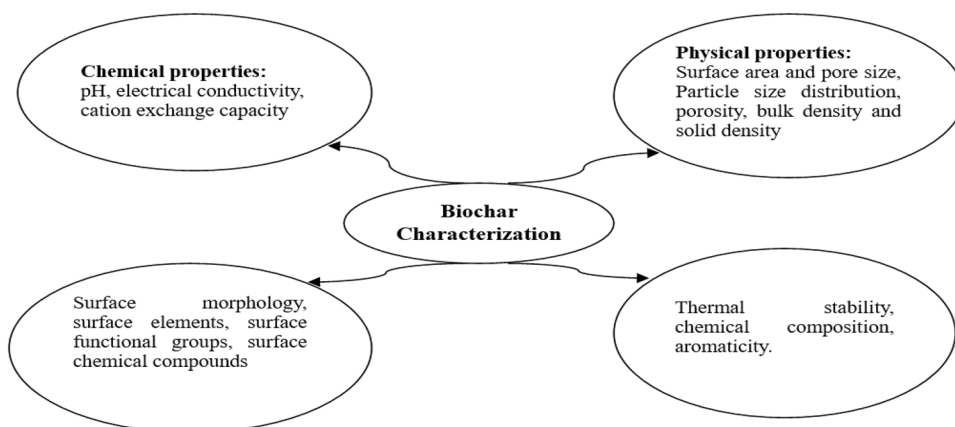


Table 3 Equations and parameters of kinetic models

Kinetic model	Proposed by	Non-linear form equation	Units and parameters description
Pseudo-first-order (PFO)	Lagergren 1898	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	q_t ($\text{mg}\cdot\text{g}^{-1}$): Amount of adsorbed solute q_e ($\text{mg}\cdot\text{g}^{-1}$): Amount of adsorbed solute at equilibrium. k_1 (min^{-1}): PFO rate constant t (min): Time
Pseudo-second-order (PSO)	Ho and McKay 1999	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$): PSO kinetic rate constant
Intraparticle diffusion (IPD)	Weber and Morris 1962	$q_t = k_3\sqrt{t}$	k_3 ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$): IPD rate constant
Elovich equation	Elovich 1939	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$): Initial adsorption rate β ($\text{g}\cdot\text{mg}^{-1}$): Elovich constant

Table 4 Equations and parameters of isotherm models

Isotherm model	Equation	Units and parameters description
Langmuir	$qe = \frac{qmKaCe}{1+KaCe}$	qe (mg g ⁻¹): Amount of adsorbate concentration in the solid phase at equilibrium qm (mg g ⁻¹): Maximum adsorption capacity Ka (L mg ⁻¹): Affinity constant Ce (mg L ⁻¹): Amount of adsorbate concentration in the liquid phase at equilibrium
Freundlich	$qe = K_F C^n$	K _F (dimensionless): Fitting-constant n (dimensionless): Fitting-constant K _S (dimensionless): Fitting-constant
Sips	$qe = \frac{K_S C_e^{\beta_S}}{1+\alpha_S C_e^{\beta_S}}$	α _S (L mg ⁻¹): Sips isotherm model constant. β _S (dimensionless): Sips isotherm model exponent

water to improve the water quality. On the other hand, once the biochar has removed the ammonium and phosphate nutrients from the water by adsorption, the nutrient-rich biochar can be utilized in fertilizer production [56].

In general, to gain a better understanding of the performance and mass transfer mechanisms of adsorbing substances from an aqueous solution, it is necessary to consider both thermodynamic and kinetic factors. The solute consumption rate, which defines the residence time necessary for the adsorption process to occur, may be determined by analysing the kinetic model [57].

According to the literature reviewed, most research papers dealing with the adsorption of ammonium and phosphates from aqueous solutions use pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic models. The application of these models is problematic since they are empirical and lack specific physical significance, thus using these empirical kinetic models makes it impossible to investigate mass transfer mechanisms. On the other hand, there are differential kinetic models with precise physical meanings, but their solution methods are rather complex [58]. Regarding isotherm models, the constants have particular physical implications that characterize the adsorbent's maximum capacity and surface characteristics [59].

The results for ammonium and phosphate removal, a summary of the feedstock material from which the biochar was made, the conditions of pyrolysis (temperature and residence time), the recovery capacity, the modification of biochar, and authors of mentioned research are summarized in Table 5.

Comparing Tables 2 and 5 reveals that the modification of the biochar improves its adsorption capacity due to the increase in the specific surface area. Moreover, biochars prepared in different conditions and further modified with various techniques like metal oxide and metal salt modifications are also compared. It can be seen that all kinds of biochar modification (metal oxide, acid–base, ball milling, and

HCl modification) result in higher pollutant removal than achieved by biochar in the pristine form. It can be concluded that biochar modification technologies help to increase the recovery capacity by up to 24 times [62].

Based on previous research regarding the mechanisms involved in the different methods of modifying biochar to improve its adsorption capacity, it can be summarized that: In the case of metal oxide and metal salt modification, the modified biochar has a larger specific surface area than pristine or unmodified biochar. According to the results shown in the work of Yin et al., modification not only increases the average pore diameter but also enhances the number of functional groups [60]. Acid–base modification resulted in increased average pore volume, while the specific surface area decreased. This can be explained through the study of pore size: micropores were observed in the pristine biochar, which were not present in modified biochar. This implies that the modification merges the micropores into larger ones. Additionally, the number of O=H functional groups increased in modified biochar compared to the unmodified one [61]. The specific surface area can also be increased by reduction of particle size, as shown in the work of Qin et al.; they also proved that changes in the functional groups improve adsorption [63].

Biochar-based fertilizers

In general, the biochar produced from agricultural waste contains small amounts of nutrients, so these concentrations can be increased if the biochar is used for the ammonium and phosphate adsorption process. In general, several investigations have been carried out in the field of biochar-based slow-release fertilizers, which have presented excellent environmental performance because they increase both crop yield and nutrient (P and N) use efficiency; some examples of the results are shown below (Table 6).

Table 5 Results for ammonium and phosphate removal

Biochar feedstock	Conditions of manufacturing biochar	Aqueous solution conditions	Recovery substance	Recovery capacity (molecule NH_4^+ , NO_3^- , PO_4^{3-})	Modification	Recovery capacity modified biochar mg/g (NH_4^+ , NO_3^- , PO_4^{3-})	Isotherm and kinetic models	References
Soybean straw	Pyrolysis 500 °C for 120 min	Synthetic solutions with initial concentration of 50 mg/L of NH_4^+ , NO_3^- , PO_4^{3-}	NH_4^+ NO_3^- PO_4^{3-}	0.50 NH_4^+ ~2.25 NO_3^- ~2 PO_4^{3-}	Metal oxide and metal salt modification using Al and Mg	0.70 NH_4^+ 40.63 NO_3^- 74.47 PO_4^{3-}	NH_4^+ Intraparticle diffusion NO_3^- Pseudo second order PO_4^{3-} Pseudo first order and Pseudo second order	[60]
Corn cob	Pyrolysis 400 °C for 60 min	Synthetic solution with initial ammonium concentration range of 10–100 mg/L	NH_4^+	3.93 NH_4^+	Acid–base modification HNO_3 , NaOH	22.6 NH_4^+	Not mentioned isotherm model Pseudo second order Sips isotherms	[61]
Sugarcane crop harvest residue	Pyrolysis 550 °C for 60 min	water solution containing dissolved organic matter was prepared from sodium humate with initial concentration of 50mg/L of each substance	PO_4^{3-} NH_4^+ Organic matter humate	<5 PO_4^{3-} ~20 NH_4^+ <10 humate	Metal oxide MgO	398 PO_4^{3-} 22 NH_4^+ 247 humate	Pseudo second order Langmuir isotherm	[62]
Bamboo	Pyrolysis 450 °C residence time not mentioned	Synthetic solution with initial ammonium concentration range of 0–100 mg/L	NH_4^+	7 NH_4^+	Ball milling modification	22.9 NH_4^+	Pseudo second order Langmuir isotherm	[63]
Wheat straw	Pyrolysis 450 °C residence time not mentioned	Synthetic KNO_3 and KH_2PO_4 solutions (the concentration of nitrogen and phosphorus was 50 mg/L) were prepared	NO_3^- PO_4^{3-}	Not mentioned	Activated with HCl, and coated with iron [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$]	2.47 NO_3^- 16.58 PO_4^{3-}	Kinetic model is not mentioned PO_4^{3-} Langmuir NO_3^- Freundlich	[64]

Table 5 (continued)

Biochar feedstock	Conditions of manufacturing biochar	Aqueous solution conditions	Recovery substance	Recovery capacity (molecule NH_4^+ , NO_3^- , PO_4^{3-})	Modification	Recovery capacity modified biochar (molecule NH_4^+ , NO_3^- , PO_4^{3-})	Isotherm and kinetic models	References
Poplar chips	Pyrolysis 300 °C under N_2 atmosphere for 120 min	Synthetic KNO_3 and KH_2PO_4 solutions (the concentration of nitrogen and phosphorus was 50 mg/L) were prepared	NH_4^+ PO_4^{3-}	1.52 NH_4^+ negative value for PO_4^{3-}	Metal oxide modification using Mg	2.45 NH_4^+ $\sim 5 \text{ PO}_4^{3-}$	Intraparticle diffusion model fitted better with pristine biochar and Pseudo second order model fitted better with modified biochar. Langmuir isotherm	[65]
Poplar chips	Pyrolysis 600 °C under N_2 atmosphere for 120 min	Synthetic KNO_3 and KH_2PO_4 solutions (the concentration of nitrogen and phosphorus was 50 mg/L) were prepared	NH_4^+ PO_4^{3-}	0.35 NH_4^+ $\sim 3 \text{ PO}_4^{3-}$	Metal oxide modification using Mg	0.72 NH_4^+ 44.4 PO_4^{3-}	Pseudo second order model Langmuir–Freundlich isotherm	[65]
Rape straw	Pyrolysis 300 °C under argon atmosphere for 30 min	Synthetic Ammonium phosphate solution with an initial concentration of 50 mg/L P (corresponding to 67.85 mg/L N) were prepared	NH_4^+ PO_4^{3-}	$\sim 3.1 \text{ NH}_4^+$ $\sim 0.5 \text{ PO}_4^{3-}$	Metal oxide/hydroxide modification using red mud	$\sim 3.3 \text{ NH}_4^+$ $\sim 1.7 \text{ PO}_4^{3-}$	Pseudo-second-order kinetic model Langmuir isotherm model	[66]
Rape straw	Pyrolysis 750 °C under argon atmosphere for 30 min	Synthetic Ammonium phosphate solution with an initial concentration of 50 mg/L P (corresponding to 67.85 mg/L N) were prepared	NH_4^+ PO_4^{3-}	$\sim 1.5 \text{ NH}_4^+$ $\sim 1 \text{ PO}_4^{3-}$	Metal oxide/hydroxide modification using red mud	$\sim 2.75 \text{ NH}_4^+$ $\sim 9.5 \text{ PO}_4^{3-}$	Pseudo-second-order kinetic model Langmuir isotherm model	[66]

Table 6 Results for the use of biochar-based fertilizers

Biochar feedstock	Conditions of manufacturing biochar	Fertilizer type	Type of plant fertilized	N or P release	Results shoot dry mass (SDM) (g/pot)	References
Corn stover	Pyrolysis 500 °C for 30 min	Biochar-based P	Spinach (<i>Spinacia oleracea</i>)	Bioavailable P release 40% after 5 days	~ 15	[67]
Coffee husk	Pyrolysis 500 °C for 120 min	Biochar-based P	Mombasa grass (<i>Megathyrsus maximus</i>) maize, and common bean	Total P release 6.47% in the first hour	Mombasa grass (second crop cycle) ~ 24 Maize ~ 12	[55]
Cotton straw	Modified biochar with bentonite and $Mg_3(PO_4)_2$. Pyrolysis 550 °C for 120 min under N_2 atmosphere	Biochar-based P	Peppers	P utilization efficiencies after 60 days	Common bean ~ 28 Not mentioned as g/pot fresh weight (~ 350 g) dry weight (~ 70 g) for pepper seedlings fertilized	[68]
Rice hull	Pyrolysis 400–500 °C for 240 min under N_2 atmosphere	Biochar-based N	Not applied to plants. Batch Experiment for nutrient leaching test were performed	Total water-soluble accumulative NH_4^+ -N and PO_4^{3-} -P were 13.8 mg/g and 44.6 mg/g after 84 days	–	[69]
Straw and wheat shell	Pyrolysis 500–600 °C for 180 min under	Biochar-based N	Not applied to plants. Leaching experiments in soil were performed	The accumulative release of N and P after 84 days was 10.62% and 6.84% in distilled water, and 59.32% and 59.12% in citric acid solution	–	[70]

Conclusion

It has been demonstrated that biochar is a promising material for water treatment. Previous studies have proved the high efficiency of ammonium and phosphate removal from water by biochar adsorption. This review emphasizes the necessity of utilizing engineered biochar for ammonium and phosphate removal. The modification of biochar's surface properties using various techniques and methods is expected to alter its surface area, surface charge, functional groups, and pore volume.

Biochar production from biomass waste materials would not compete for land with any other land use choice, including food production or maintaining the land's natural state, thereby addressing at least two of the most pressing environmental concerns.

The literature highlights the relevance of research focusing on biochar's sorption mechanism, desorption, and sorption kinetics for removing organic compounds and heavy metals from aqueous solutions, making biochar a promising technology for wastewater treatment. A further promising opportunity for use is the degradation of organic pollutants by catalytic reactions.

Further research is required to establish a highly efficient and cost-effective technology for modifying biochar, increasing its practical application in wastewater treatment and enhancing its adsorption capacity for nitrogen and phosphorus, heavy metals, and organic pollutants.

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