



Review Research Progress on Adsorption of Arsenic from Water by Modified Biochar and Its Mechanism: A Review

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Abstract: Arsenic (As) is a non-metallic element, which is widely distributed in nature. Due to its toxicity, arsenic is seriously harmful to human health and the environment. Therefore, it is particularly important to effectively remove arsenic from water. Biochar is a carbon-rich adsorption material with advantages such as large specific surface area, high porosity, and abundant functional groups, but the original biochar has limitations in application, such as limited adsorption capacity and adsorption range. The modified biochar materials have largely enhanced the adsorption capacity of As in water due to their improved physicochemical properties. In this review, the changes in the physicochemical properties of biochar before and after modification were compared by SEM, XRD, XPS, FT-IR, TG, and other characterization techniques. Through the analysis, it was found that the adsorbent dosage and pH are the major factors that influence the As adsorption capacity of the modified biochar. The adsorption process of As by biochar is endothermic, and increasing the reaction temperature is conducive to the progress of adsorption. Results showed that the main mechanisms include complexation, electrostatic interaction, and precipitation for the As removal by the modified biochar. Research in the field of biochar is progressing rapidly, with numerous achievements and new types of biochar-based materials prepared with super-strong adsorption capacity for As. There is still much space for in-depth research in this field. Therefore, the future research interests and applications are put forward in this review.

Keywords: biochar; arsenic; adsorption; mechanism; modification; water treatment

1. Introduction

Arsenic, the silent poison, is odorless and tasteless when dissolved in water, and is named 'King of Poisons' and 'Poisons of King' [1]. Arsenic in water mainly exists as inorganic arsenate (As(V)) and arsenite (As(III)) and varies with water concentration. Under oxidizing and aerobic conditions, As(V) is dominant, and its main form is arsenate oxygenated anions ($H_2AsO_4^-$ and $HAsO_4^{2-}$). The toxicity of As (III) is significantly stronger than that of As(V) [2,3]. Long-term exposure to arsenic will lead to arsenic poisoning, which may include multiple organ diseases. Inorganic arsenic will result in skin, vascular and nervous system disorders and cancer. For example, in Bangladesh, arsenic pollution in groundwater is a very serious problem. It is reported that in addition to the manifestations of skin diseases, non-communicable diseases, including cancer adverse pregnancy outcomes and the decline of children's IQ are increasing significantly in this area [4,5]. The World Health Organization (WHO) has established standards for arsenic in drinking water at 10 mg/L. However, Podgorski and Berg [4] estimated that around



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 94–220 million people may be exposed to high levels of arsenic in groundwater, with the vast proportion (94%) in Asia. Arsenic contamination was referred to as a disaster of the 20th to 21st centuries by researchers and authorities. Due to the harmful effects of arsenic on human health and the environment, effective remediation of arsenic-contaminated water remains a critical task.

Researchers have employed a variety of methods to eliminate arsenic contamination. Currently, common arsenic removal methods include the physical method (ion exchange, membrane technology, and adsorption), chemical method (chemical precipitation and electrokinetic technology), and biological method (phytoremediation) [6,7]. The advantages of chemical methods are high efficiency and rapidity. However, this method produces vast volumes of sludge and requires high-energy costs and economic costs [8,9]. Phytoremediation is eco-friendly with less by-product production, but it is a time-consuming process and requires specific care and strict control [10], so is not suitable for large-scale application [7]. Ion exchange and membrane technology have high regeneration and selectivity, while the initial capital cost and maintenance cost is high [6,11]. including adsorbent porous membranes [12,13] and electrocoagulation [14–16] which is an electrochemical technique. Among them, adsorption is low cost, has few by-products, simplicity in operation, and is easily available. The utilization of the adsorption method gives a sustainable cost-effective solution for arsenic contamination remediation [17,18].

At present, an assortment of adsorbents have been utilized to eliminate arsenic from water, such as activated carbon [19,20], granular ferric hydroxide [21], magnetic graphene oxide [22], iron oxide [23–25], zeolite [26], nanocomposite [27], ion exchange resins [28], and biochar [29]. Biochar is a carbon-rich material, which is a biomass material prepared by thermal decomposition of solid waste at low temperature (usually temperature < 900 °C) under anoxic or anaerobic conditions [30,31]. It has attracted extensive attention because of its wide source of raw materials, low cost, large specific surface area, also its pore volume, stable structure, rich active functional groups, and strong adsorption capacity [32], which has broad application prospects in the expulsion of arsenic in water. Among the many adsorbents mentioned above, activated carbon is also a carbon-rich material. However, there are an extensive number of negatively charged functional groups on the surfaces of activated carbon, which is not an effective adsorbent for As [33], and according to the comparative analysis of biochar and activated carbon by Alhashimi and Aktas [34], it can be seen that biochar is superior to activated carbon in many aspects, for example, the energy required to produce biochar is much lower than that of activated carbon, and the greenhouse gas emissions produced by the activated carbon adsorption process are higher than biochar. The environmental benefits of biochar are even greater. Therefore, biochar can be widely used as a substitute for activated carbon in water treatment. However, at the same time, the original biochar has some limitations, such as restricted adsorption capacity and tight adsorption range [35]. Therefore, many researchers focus on making modified biochar with stronger adsorption capacity to further develop its adsorption effectiveness. For example, Wang et al. [36] prepared modified corn stover biochar using potassium hydroxide and phosphoric acid. The results indicated that the surface area of acid and alkalimodified biochar expanded by 10 and 14 times respectively, and the equilibrium adsorption quantity of enrofloxacin on the two modified biochar increased by 27.80% and 54.08% respectively. Gholami et al. [37] prepared a novel Fe-Cu layered double hydroxide/biochar nanocomposite by hydrothermal synthesis. It was found that compared with BC, the total pore volume of Fe-Cu-LDH/BC expanded from $0.75 \text{ cm}^3/\text{g}$ to $0.89 \text{ cm}^3/\text{g}$ and the specific surface area expanded from 78.63 m^2/g to 91.35 m^2/g . When the temperature reached 80 °C, the adsorption of cefazolin sodium (CFZ) on Fe-Cu-LDH/BC (32.6%) exceeded that of Fe-Cu-LDH (15.5%) and pure BC (24.6%), and the efficiency of biocatalytic degradation of cefazolin sodium in water reached 97.6%. Li et al. [38] prepared an iron-based composite adsorbent based on biochar by co-precipitation and sol-gel method. The removal efficiency of Hg⁰ by single iron-based modified biochar, iron-based modified biochar doped with various metals (Cu, Ce, Mn, and Co), and original biochar was compared, and the results

showed that the efficiency of arsenic removal by modified biochar is significantly enhanced, and the maximum removal efficiency is 13 times that of the unmodified biochar. It can be seen that modified biochar is an adsorbent with excellent performance. So far, relevant researchers have conducted extensive research on it. Table 1 summarizes the research on arsenic removal from water using modified biochar over the past decade. Using modified biochar to remove arsenic in water has broad application prospects.

Feedstock of Modified Max.Adsorption Number **Arsenic Species** Reference Biochar Material/Method Capacity FeSO₄·7H₂O and 1 Rice straw Nham et al. (2019) [39] As (V) 26.9 mg/g FeCl₃.6H₂O Gelatin, FeCl₃ and 2 Chestnut shell As (V) 45.8 mg/g Zhou et al. (2017) [40] FeCl₂ 3 28.2 mg/g Kraft lignin FeOx, CO₂ As (V) Cha et al. (2021) [41] Electrochemical 4 Canola straw As (V) 922 µg/g Benis et al. (2021) [42] modification 5 As (III) Corn straw FeOx, MoS₂ 27 mg/g Khan et al. (2021) [43] 6 Hickory chips Fe(NO₃)₃·9H₂O As (V) 2.16 mg/g Hu et al. (2015) [44] 7 Canola straw As (V) FeCl₃ 5.5 mg/gBenis et al. (2021) [45] Poplar wood 8 FeCl₃ As (III)/As (V) 48.6 / 122.0 mg/g Feng et al. (2021) [46] particles Ferric nitrate 9 Banana pith As (V) 120.91 µg/g Lata et al. (2019) [47] nonahydrate Sewage sludge 10 KOH As (V) $8.5 \,\mu mol/g$ Wongrod et al. (2018) [48] digestate Rice straw, Fe²⁺, Fe³⁺ 17.876 mg/g Liu et al. (2017) [49] 11 As (V) Chitosan 12 AlCl₃·6H₂O 17.41 mg/g Zhang et al. (2013) [50] Cottonwood As(V)13 γ -Fe₂O₃ As(V) 429 mg/kg Wang et al. (2015) [51] Pinewood As(V)14 Loblolly pine MnCl₂·4H₂O/KMnO₄ 0.59 /0.91 g/kg Wang et al. (2015) [52] Municipal solid 15 KOH As(V) 30.98 mg/g Jin et al. (2014) [53] waste Empty fruit Fe(III) As(III)/As(V) 16 31.4/31.4 mg/g Samsuri et al. (2013) [54] bunch/rice husk 17 Pinewood FeCl₃·6H₂O As (V) 124.5 g/kg Wang et al. (2013) [55] 18 Kans grass Fe₃O₄ As(III)/As(V) 2.004/3.132 mg/g Baig et al. (2014) [56] FeCl₃·6H₂O 19 Waste walnut As(V)1.91 mg/g Duan et al. (2017) [57] 20 Corn stem KMnO₄, Fe(NO₃)₃ As(III) 8.25 mg/g Lin et al. (2017) [58] 21 Hyacinth FeCl₂, FeCl₃ As(V)7.41 mg/g Zhang et al. (2016) [59] Ni/Fe-LDH/Layered 1.56/4.38 g/kg 22 Pine As(V)Wang et al. (2016) [60] double hydroxides 108.88 mg/g 23 Wheat straws CeCl₃, KMnO₄ As(V) Liang et al. (2020) [61] 78.3 mg/g 24 Wheat straw Fe(NO₃)₃, KOH As(III) Zhu et al. (2020) [62] Fe(NO₃)₃, KOH 65.3 mg/g 25 Wheat straw As(III) Zhu et al. (2020) [63] 26 Yak dung FeCl₂ As(V) 2.926 mg/g Chunhui et al. (2018) [64] 27 Crayfish shell ZnCl₂ As(V) 17.2 mg/g Yan et al. (2018) [65]

Table 1. The reviews on arsenic in the last decade.

Biochar adsorption is a popular research field in recent years, but as far as we know, there are few comprehensive and systematic reviews on the removal of arsenic in water by modified biochar, especially the modification method and the factors affecting the arsenic removal efficiency, and the removal mechanisms. Therefore, the aims and novelty of this review are to discuss: (1) Modification methods of biochar and the influence on the physicochemical properties of biochar; (2) Characterization techniques of biochar, particularly, in addition to conventional characterization techniques, several emerging techniques for characterizing the physicochemical properties of biochar have been provided; (3) Various influencing factors of arsenic removal from water by modified biochar; (4) The removal mechanisms of arsenic by modified biochar. Finally, suggestions for future research directions are put forward.

2. Biochar Preparation and Modification

2.1. Preparation of Biochar

Biochar is a solid created by pyrolysis of biomass under anoxic or anaerobic circumstances at 300–800 °C. The raw materials used to produce biochar come from a wide variety of sources, including various solid wastes, agricultural wastes, and sludge from sewage treatment plants, such as crop straw, orange peel, animal manure, etc. The preparation process of biochar can generally be divided into the following steps: (1) Pretreatment before pyrolysis. It can be divided into physical (drying, crushing, sieving, washing, etc.), chemical (treatment with chemicals or functional materials to load chemical precursors or functional agents), and biological (bacterial treatment, etc.) technologies. Among them, biological pretreatment is a relatively new notion in recent years [66]. In biological pretreatment, anaerobic digestion treatment has been proven to obtain a larger specific surface area and higher adsorption efficiency of biochar [67]. (2) Pyrolysis. Usually, biochar is pyrolyzed after simple physical pretreatment. According to the pyrolysis time, the pyrolysis process can be classified as 'slow', 'medium', and 'fast' pyrolysis [32]. Pyrolysis is the most widely used method to prepare biochar currently. In addition, there are gasification, hydrothermal carbonization, microwave, and dry torrefaction [68]. Figure 1 briefly summarizes various preparation methods of biochar from different sources. (3) Post-pyrolysis treatment. The post-treatment technology of biochar is to increase the specific surface area and pore volume of biochar by physical or chemical modification [61], which is commonly referred to as modification; details will be described in Section 2.2.



Figure 1. Summary of various preparation methods of biochar [68]. Reprinted with permission from Yuxin Jiao et al. (2021). Copyright 2021, Springer.

The raw materials of biochar, pyrolysis temperature, the residence time of pyrolysis, and heating rate will affect the physicochemical properties of biochar. Biochar produced from animal manure and sludge has higher yields, due to them containing more inorganic components [69], but some metal components contained in them will prevent the release of volatile substances, which will reduce the specific surface area and quantity of active sites of biochars [32]. The biochar under slow pyrolysis was mineralized 10 to 18 times slower

than feedstock, which indicates that biochar has high C-sequestration potential [70], which has a significant effect on the aromaticity and stability of biochar. Among the products of pyrolysis, there is a polar-low-molecular weight organic fraction (bio-oil) with high water content. With the increase of the pyrolysis temperature, a large amount of volatiles will be released into the bio-oil and natural gas fractions, thereby reducing the production of biochar [71]. The yield of biochar decreased with increasing pyrolysis temperature, while the ash and carbon contents increased [32]. Table 2 lists the physicochemical properties of some biochars prepared from diverse raw materials at different temperatures.

Feedstock	Pyrolysis Temp. (°C)	Ash (%)	pН		Element C	Content (%)	Specific Surface	Pore Volume		
				С	Н	0	Ν	- Area (m ² /g)	(cm ³ /g)	Reference
Peanut shell	300	1.24 ± 0.08	7.76 ± 0.06	68.27	3.85	25.89	1.91	3.14	/	Ahmad et al. (2012) [72]
	500	/	/	/	/	/	/	0.7447	0.002651	An et al. (2019) [73]
	700	17.18 ± 0.25	10.57 ± 0.05	83.76	1.75	13.34	1.14	448.2	0.20	Ahmad et al. (2012) [72]
Soybean stover	300	10.41 ± 0.52	7.27 ± 0.03	68.81	4.29	24.99	1.88	5.61	/	Ahmad et al.
	700	17.18 ± 0.25	11.32 ± 0.02	68.81	1.27	15.45	1.30	420.3	0.19	(2012) [72]
Hardwood	450	38.55	5.57	53.41	2.30	5.67	0.07	0.43	0.00036	Chen et al. (2011) [74]
Corn straw	600	60.19	9.54	35.88	1.64	1.86	0.43	13.08	0.014	Chen et al. (2011) [74]
Dairy manures	500	90	10	1.67 ± 0.4	/	/	0.04 ± 0.01	13	/	Cao et al. (2010) [75]
Orange Peels	300	1.57	/	69.3	4.51	22.2	2.36	32.3	0.0313	
	350	2.00	/	73.2	4.19	2.30	18.3	51.0	0.0098	
	400	2.10	/	71.7	3.48	20.8	1.92	34.0	0.0099	Chen et al.
	500	4.27	/	71.4	2.25	20.3	1.83	42.4	0.0191	(2010) [76]
	600	4.04	/	77.8	1.97	14.4	1.80	7.78	0.0083	
	700	2.79	/	71.6	1.76	22.2	1.72	201	0.0350	
Chialan manage	350	38.21 ± 2.75	8.21 ± 0.06	38.11 ± 0.46	3.40 ± 0.03	55.91 ± 4.06	2.59 ± 3.63	/	/	
Chicken manure	650	48.76 ± 2.38	9.96 ± 0.02	32.56 ± 0.27	0.91 ± 0.10	65.08 ± 0.19	1.46 ± 0.18	/	/	
Sugarcane straw	350	24.22 ± 2.07	8.67 ± 0.03	60.13 ± 5.96	2.44 ± 0.16	35.78 ± 7.07	1.66 ± 0.95	/	/	
	650	13.32 ± 1.54	9.17 ± 0.05	69.37 ± 1.91	2.45 ± 0.95	26.69 ± 3.08	1.50 ± 2.11	/	/	Higashikawa et al.
Rice husk	350	40.44 ± 0.29	8.44 ± 0.08	32.79 ± 7.99	1.09 ± 0.35	66.09 ± 8.32	0.04 ± 0.02	/	/	(2016) [77]
	650	41.97 ± 0.27	8.72 ± 0.06	49.48 ± 1.70	1.47 ± 0.06	49.04 ± 1.75	0.02 ± 0.01	/	/	
C 1 (350	1.24 ± 0.22	7.59 ± 0.17	49.04 ± 1.75	3.94 ± 0.06	24.35 ± 0.40	0.10 ± 0.12	/	/	
Sawuusi	650	1.19 ± 0.11	7.48 ± 0.02	84.60 ± 1.15	2.84 ± 0.39	12.35 ± 1.05	0.22 ± 0.29	/	/	
Cacao shell	350	17	10.42	70	1.6	/	1.4	18.6	0.0147	Hale et al.
Corn cob	400	13	8.97	66	2.6	/	0.6	36.4	0.0222	(2013) [78]
Platanus orientalis L.	650	9.7	9.3	69.3	2.7	/	1.1	/	/	Yang et al. (2022) [79]
Rice straw	300	/	8.2 ± 0.01	53.5 ± 0.2	3.7 ± 0.1	/	1.5 ± 0.1	/	/	
	550	/	10.5 ± 0.1	59.8 ± 0.4	1.7	/	1.3 ± 0.1	/	/	
	700	/	10.3 ± 0.1	60.8 ± 0.4	1.2 ± 0.1	/	1.2 ± 0.1	/	/	$V_{im} = 1 (2010) [00]$
Granular sludge	300	/	7.8 ± 0.1	53.5 ± 0.2	5.8 ± 0.1	/	9.0	/	/	Kiiit et al. (2010) [80]
	550	/	9.5 ± 0.1	48.0 ± 0.2	1.8 ± 0.1	/	6.9	/	/	
	700	/	9.7 ± 0.1	50.5 ± 0.4	1.0 ± 0.1	/	6.5 ± 0.1	/	/	

Table 2. Physicochemical properties of biochar prepared from diverse raw materials.

2.2. Modification of Biochar

Since the original biochar surface is usually negatively charged, static resistance exists between the oxyanions of arsenic and the negatively charged biochar surface which is not conducive to its adsorption [81]. As a result, biochar must be modified to improve arsenic removal effectiveness. For example, the surface of biochar can be positively charged by Metal oxide and metal salt modification. In addition, although the original biochar has a large specific surface area and porosity, and rich functional groups, its adsorption capacity, and adsorption efficiency are limited. However, the physicochemical properties of the original biochar can be enhanced through modification, which further enhances its adsorption capacity and adsorption efficiency for As. Biochar modification will change the shapes and size distributions of the pores as well as the specific surface area and surface functional groups. Furthermore, different modification processes and modifiers may have varying effects on biochar's physicochemical properties. These changes will have a direct impact on the effectiveness of arsenic adsorption [35].

The modification of biochar is generally divided into pre-pyrolysis modification and post-pyrolysis modification. Pre-pyrolysis modification is the application of physical or chemical methods to the raw materials, while post-pyrolysis modification is more common [82]. The following techniques are generally used to modify the biochar: steam physical activation [82], chemical activation using acidic and alkaline solutions, metal oxide and metal salt modification, clay mineral modification, and ball milling modification [35]. Figure 2 sums up the current grouping framework for the most well-known modification methods.



Figure 2. A grouping framework of biochar modification methods [82]. Reprinted with permission from Tom Sizmur et al. (2017). Copyright 2017, Elsevier.

In the process of steam physical activation, the surface of biochar is corroded and additional syngases are released (mostly in the form of hydrogen [83]) due to high temperature, which changes the surface morphology of biochar and increases the surface area of biochar. At the same time, steam activation will remove trapped particles or volatile gases, allowing the biochar to form internal pores, thereby increasing the pore volume [84]. Sewu et al. [85] used this method to improve the texture properties of spent mushroom substrate biochar. They found that the specific surface area of the steam-activated biochar (SA-BC) expanded by 267.6 m²/g, the pore volume increased by 0.24 cm³/g, and the porosity in SA-BC (77.1%) was also higher than BC (67.5%). However, steam activation has little effect on pore size because it remains relatively stable in the mesoporosity range. The biochar after steam activation has low H/C and O/C, which indicates that it is not suitable for enhancing the surface functionality of biochar [84]. Moreover, Bardestain and Kaliaguine [86] also found that steam activation increases the content of fixed carbon in the biochar because of the thermal degradation of volatile components, and an increase also in the ash content.

The chemical activation method exposes biochar to acidic or alkaline solutions, which will oxidize the surface to form oxygen-containing functional groups [87], and the physicochemical properties of biochar will also be affected, such as hydrophilicity, ion exchange capacity, expanding the SSA, and increasing the pore structure of the biochars, and enhanced adsorption capacity [35,88]. The several various chemicals commonly used are summarized in Figure 3.



Figure 3. Several chemicals commonly used to modify biochar [89]. Adapted with permission from KhaledZoroufchi Benis et al. (2020). Copyright 2020, Elsevier.

Chemical modification is better than physical modification because it can increase the number of functional groups on the biochar's surface after modification [90]. Acid treatment will increase the carboxyl group on the surface of biochar, making it more conducive to the adsorption of cations, and alkali treatment can increase the content of hydroxyl groups on the surface and enhance its ability to adsorb anions [82]. Besides, compared with acid modification generated negative charges on its surface, alkali modified biochar has good performance that attracted As oxyanions, which was suggested to be due to a large number of positive charges generated [81]. Sewage sludge digestate was utilized to produce biochar for As(V) removal by Wongrod et al. [48]. The biochar was modified in a 2 M KOH solution. Results showed that the BET surface area of the modified biochar (BKOH) was obviously expanded, from 0.4 (\pm 0.1) to 7.9 (\pm 0.1) m²/g, indicating that the porosity of the biochar increased, making it more favorable for As adsorption, and the Q_m values being 5 times higher than that of the raw biochar, and the increase of pH_{pzc} of BKOH increases the number of positive charges on the surface of biochar, thereby enhancing the adsorption of As(V) anions. In addition, they found that although the BKOH enhanced the adsorption capacity of As, its kinetic process was slow. Hussain et al. [91] compared the efficiency of cotton stalk biochar modified with KOH and H₃PO₄ respectively to remove As in water, and observed by FT-IR spectroscopy that aromatic, alcoholic, phenolic, and amide groups all assume a part in the adsorption process. The experimental results show that under the conditions of optimal dosage (2 g/L) and pH (5), compared with original biochar and acid-modified biochar, alkali-modified biochar had the best As removal effect (90–99%) due to its higher specific surface area, larger porosity, and the diminished particle size of the biochar.

Metal oxide and metal salt were used to introduce new functional groups on the surface of biochar and enhance the As adsorption capacity. The surface of biochar is usually negatively charged and has a high pH value [81], while As usually exists in the form of oxyanion in an aqueous solution [31], so the reaction is carried out by soaking biochar in the metal oxide or metal salt solution (usually positive charge). On the one hand, new functional groups are introduced, and on the other hand, the positive charge on the surface of biochar is increased, resulting in the enhancement of the adsorption capacity of As oxyanions through electrostatic attraction. According to the different characteristics of metal oxides or metal salts, biochar has different adsorption capacities for As. Metal oxides or metal salts commonly used in modified biochar include hematite (γ -Fe₂O₃), magnetite, hydrous Mn oxide, calcium oxide, Fe⁰, FeCl₃, Fe(NO₃)₃, MgCl₂, ZnCl₂, and so on. Interestingly, the specific surface area of the biochar is reduced because of the stopping up of the pores due to metal ingress, and the internal pore structure of the biochar is changed [92]. However, the effect of this phenomenon on As adsorption is negligible, owing to the adsorption of As on metal-impregnated biochar being mainly controlled by the chemisorption mechanism. As reported by Hu et al. [44], Fe-impregnated hickory biochar was synthesized by direct hydrolysis, and the specific surface area of the Fe-impregnated biochar was significantly reduced $(16.0 \text{ m}^2/\text{g})$ contrasted with the original biochar ($256 \text{ m}^2/\text{g}$). However, Fe-impregnated biochar exhibited higher As adsorption capacity, and the maximum adsorption capacity reached 2.16 mg/g when the pH was around 5.8. According to Wang et al. [51], the specific surface area of pine biochar modified with hematite (γ -Fe₂O₃) decreased from 209.6 m²/g to 193.1 m²/g, and the adsorption capacity for As was roughly double that of the unmodified one (429 mg/kg and 265 mg/kg, respectively). This is basically because both the functional groups on the biochar surface and loaded iron oxide particles can be used as adsorption sites for As. The magnetic modification of biochar is also a research hotspot in this field in recent years, not only because the magnetic modification can increase the adsorption capacity of As by biochar, but also because magnetic biochar can be easily separated with outside magnets [51], or separated and recovered from aqueous solutions by adding a certain magnetic field [93]. For example, He et al. [94] used FeCl₃ solution to impregnate corn stover biochar to explore the adsorption efficiency of $A_{S}(V)$, and the results showed that the adsorption efficiency of the modified biochar (6.80 mg/g) was 400 times higher than that of the unmodified (0.017 mg/g), and the FBC with a mass ratio of 20% exhibited high saturation magnetization with a value of 67.2 emu/g at 300 K, the As-loaded biochar can be easily separated from the solution using a permanent magnet. Tian et al. [95] synthesized different contents of magnetic wheat straw biochar (MWS) by in situ co-precipitation method (iron ion concentrations were MWS₁: 0.1 mol/L, MWS₂: 0.2 mol/L, MWS₅: 0.5 mol/L, respectively), the characteristic peaks of Fe_3O_4 appear in the XRD pattern indicates that Fe_3O_4 has been successfully loaded on the biochar. The hysteresis loops are shown in Figure 4, and they all exhibit typically super-paramagnetic behavior and the saturation magnetizations are MWS₁: 6.18 emu/g, MWS₂: 9.12 emu/g, MWS₅: 11.87 emu/g, the adsorption capacity of As(V) is higher than that of As(III), and the adsorption capacity is in the order of $MWS_5 > MWS_2 > MWS_1$. Zhou et al. [40] used magnetic gelatin to modify chestnut shell biochar to remove As(V) in wastewater, and the saturation magnetization of MG-CSB was detected to be 42 emu/g. It indicates that Fe_3O_4 has been effectively loaded onto the surface of MG-CSB. At the optimum pH (4.0), the maximum adsorption amount of As was 45.8 mg/g, which was much higher than that of the original biochar. A large number of studies show that good adsorption capacity for As is obtained with an easy separation from the water of magnetic biochar [50,96–100].





Clay mineral modification is used to combine clay minerals with biochar to make biochar/clay mineral composites. The surface area and porosity of biochar are increased [101,102], and the most commonly used clay mineral is montmorillonite. Clay mineral modification changes the elemental composition of biochar and introduces new metal elements such as Fe and Al [103]. Ball milling is a method of manufacturing nanomaterials. The particle size of biochar can be reduced to the micron or even nanometer through the high-speed spheres of the ball mill [104]. Yuan [105] found that the specific surface area of pristine biochar was increased by 200 times using a dry ball milling process. Therefore, ball milling modification also improves the adsorption capacity of biochar by increasing its specific surface area and porosity. The grinding time has a great influence on the surface area of biochar. A short grinding time will help biochar to form finer particles and increase the specific surface area, while a long grinding time will cause agglomeration between particles [106]. In addition, the choice of grinding media may introduce different new functional groups into the biochar [35]. Among all biochar modification methods, ball milling modification is considered a green technology [106] but so far, there are relatively few studies on the removal of As in water by this method.

3. Characterization of Biochar

3.1. SEM Analysis

A scanning electron microscope (SEM) has been extensively applied to various fields to characterize the microscopic morphology of materials. It can observe the changes in the apparent morphology before and after biochar modification. In addition, SEM can also be combined with Energy Dispersive Spectroscopy (EDS) to analyze the elemental composition of biochar. Zhu et al. [107] analyzed the morphology and particle size of bismuth-impregnated wheat straw biochar prepared at different temperatures (400 °C, 500 °C, 600 °C) by SEM (Figure 5). The pore structure of CBC 500 is inerratic, while CBC 600 has an unordered pore structure, and although the surface of CBC 400 is rougher than the other, the porosity is poor, after carbonization of modified biochar, spherical particles will be embedded on the porous surface of biochar, and it can be seen from Figure 5 that the pore size of biochar surface decreases with the increase of carbonization temperature. In addition, some larger particles are attached to the surface of BiBC600, and its surface is uneven. The biochar modified by $ZnCl_2$ also showed more pore structure than the original biochar [108]. The surface of biochar impregnated with iron-manganese oxide is uneven and has irregular fixtures, which may be caused by the filling of iron-manganese

oxide. Combined with EDS mapping, it shows that there are peaks of Fe and Mn, which also confirms that the corresponding oxides are successfully loaded on the surface of biochar [109]. The SEM of Fe-impregnated mill sludge biochar shows that it has irregularly shaped microscale aggregates, according to EDS results, these aggregates are composed of 12.43 wt% C, 33.85 wt% O, 38.73 wt% Fe, 11.27 wt% Ca and 2.8 wt% S [110]. In summary, the modified biochar has a rough surface and pore structure, which provides favorable conditions for the adsorption of As.



Figure 5. SEM images of wheat straw prepared at various temperatures before and after modification (modified from [107]). Reprinted with permission from Ningyuan Zhu et al. (2016). Copyright 2016, Elsevier.

3.2. XRD Analysis

The crystal structure of biochar can be determined by X-ray diffraction (XRD) technique, and the mineral information contained in the biochar can be obtained [111]. For example, Wang et al. [55] found that there are characteristic peaks of metallic Fe (Fe⁰) ($2\theta = 44.5^{\circ}$) on the XRD patterns of both nZVI and newly prepared nZVI/BC, corresponding to d-spacing = 2.027 Å, and the presence of 2.95 Å indicates the presence of maghemite (γ -Fe₂O₃), possibly the amorphous iron oxides on nZVI/BC and nZVI. The XRD patterns of the original biochar and ZnCl₂ modified biochar are shown in Figure 6 [108]. It was found that the mineral strength of ZnCl₂ modified biochar was slightly reduced, but the biochar structure did not change, and it was observed that CaZn₂ (PO₄)(H₂O), Zn(OH)(NO₃)(H₂O), and Zn₂(SiO₄) peaks appeared. The results also showed that Zn mainly existed on the surface of biochar in the form of Zn-OH. Cruz et al. [112] investigated the crystal structures of coffee husk biochar (CH-B, CH-ZnO) and corncob biochar (CC-B, CC-ZnO) before and after ZnO impregnation by XRD (Figure 7), the images of CC-B and CH-ZnO show amorphous features, and CC-ZnO show a combination of amorphous and crystalline structures (marked with *), which indicates that crystalline ZnO exists only in CC-ZnO.

3.3. XPS Analysis

X-ray photoelectron spectroscopy (XPS) was used to determine the type and percentage of elements of biochar and is likewise used to distinguish functional groups on the surface of biochar [113]. Wang et al. [55] found that the content of Fe in the nano-zero-valent iron-modified biochar (nZVI/BC) was 131 times that of the original pine biochar by XPS, increasing from 0.08% to 10.5%, which confirmed the sharp increase of Fe after modification. To understand the elemental information on the surface of Fe impregnated mill sludge biochar (PMSB), Yoon et al. [110] showed peaks on the C1s, O1s, N1s, and Fe2p3 spectra, on the C1s spectrum, the peaks at the two binding energies of 284.68 eV and 290.1 eV corresponded to C–C and CO_3^{2-} , respectively, while on the O1s spectrum, the presence of carboxyl groups in biochar was discovered to be due to the peak at 531.88 eV, the binding energy of 398.58 eV and 400.58 eV in the N1s spectrum produced two peaks, representing C–N and C=N, respectively, while the peaks at 711.18 eV and 724.88 eV were observed in the Fe2p XPS spectrum, correspond to the 2p3/2 binding energy of Fe₃O₄. The XPS results of the biochar/ γ -Fe₂O₃ composite (Figure 8) show that the binding energies of Fe2p1/2 and Fe2p3/2 are 723.76 eV and 710.43 eV, respectively, which are similar to the value of Fe (III) compounds in previous studies [114]. This indicates that the iron oxides in the biochar matrix are γ -Fe₂O₃ particles. The result indicated that the γ -Fe₂O₃ was successfully loaded on the surface of biochar [115].



Figure 6. XRD patterns of pristine biochar, Zn-modified biochar, and ZnCl₂-modified biochar after adsorption of As(III) [108]. Reprinted with permission from Dong Xia et al. (2016). Copyright 2016, Elsevier.



Figure 7. Diffraction pattern of XRD patterns of CH-B, CH-ZnO, CC-B, and CC-ZnO [112]. (* shows a combination of amorphous and crystalline structures). Reprinted with permission from G.J.F.Cruz et al. (2020). Copyright 2020, Elsevier.



Figure 8. Shirley background-subtracted Fe2p1/2 and Fe2p3/2 XPS spectra of biochar/ γ -Fe₂O₃ composite [115]. Reprinted with permission from Ming Zhang et al. (2012). Copyright 2012, Elsevier.

3.4. FT-IR Analysis

The characteristics of the functional groups of the biochar can be obtained by the Fourier Transform infrared spectroscopy (FT-IR) spectra. It can also reflect the functional group changes of biochar before and after As adsorption [113]. For instance, Cruz et al. [112] showed the FR-IR spectra of the four biochars of coffee husk biochar (CH-B, CH-ZnO) and corncob biochar (CC-B, CC-ZnO) before and after ZnO impregnation, and found that there were similar functional groups which are aromatic C-H group, C-O (hydroxyl functional group attached to a carbon atom) and/or ether group C-O-C, C=C, and carbonyl C=O, corresponding to the peak at 880 cm⁻¹, 1100 cm⁻¹, 1560 cm⁻¹, and 1700 cm⁻¹ in Figure 9, respectively. Figure 10 shows the FT-IR spectra of the original biochar and Zn-modified biochar. The peak appeared between 1900 cm⁻¹ and 800 cm⁻¹, and the functional groups contained mainly included ketone, aldehyde, lactones or carboxyl groups (1614.20 cm^{-1}), aromatic rings, or rings with C=C bonds (1517.78 cm⁻¹, 450.28 cm⁻¹), the peaks between 1203.42–1072.28 cm⁻¹ are due to the presence of C–O stretching groups of carboxylic acids or on account of the coupling of the C-N stretching band and the N-H bending band, the C–H aliphatic or aromatic bonds correspond to peaks between 900 and 800 cm^{-1} , while the large peak at 3434.34 cm⁻¹ owing to the O–H stretching vibration of hydrogen bonds. The peak at 2929.4 cm^{-1} represents an aliphatic C–H group. The disappearance of the peak at 1220.78 cm^{-1} is due to the modification of biochar, but multiple peaks appeared between 1203.42 cm⁻¹ and 172.28 cm⁻¹. At the same time, additional N=O adsorption is observed [116]. Nham et al. [39] studied the FT-IR spectra of iron-impregnated biochar and pristine straw biochar and found that both of the biochar surfaces have C=O and C–O adsorption peaks, which were ascribed to carboxyl and lactone functional groups, respectively. The Fe–O peak vibration of iron-modified biochar appeared at 782 cm⁻¹. The properties can enhance the functional group strength on the polymer surface, which provides new active sites for biochar adsorption. Bashir et al. [117] also found that the functional adsorption groups on the surface of the modified straw biochar increased compared to the original biochar, such as newly generated –COOH.



Figure 9. FT-IR spectra of CH-B, CH-ZnO, CC-B, CC-ZnO [112]. Reprinted with permission from G.J.F.Cruz et al. (2020). Copyright 2020, Elsevier.



Figure 10. The FT-IR spectra of raw and Zn-loaded pine cone biochar [116]. Reprinted with permission from N. Van Vinh et al. (2015). Copyright 2015, Springer.

From the above analysis, we deduced that the modification of biochar can increase the number of oxygen-containing functional groups on the surface of biochar, and generate more active sites for biochar in the adsorption process. The increase in the type and number of functional groups can provide the maximum coordination affinity with heavy metals [117], and improve the adsorption efficiency of biochar. Since functional groups assume a vital part in As adsorption, FT-IR is a method to characterize the functional groups of biochar, which are essential for analyzing the adsorption mechanism of As on biochar.

3.5. TG Analysis

By analyzing the thermogravimetric curve, the change in thermal stability of biochar before and after modification can be obtained. For example, Xia et al. [108] compared the thermal stability of biochar residues and the biochar prepared by biogas residues and ZnCl₂-impregnated biochars. From Figure 11, it can be seen that the original biochar did not decompose until the temperature reached 400 °C, indicating that it has strong thermal stability. But the weight of biochar dropped sharply between 400 °C and 550 °C, indicating that it still has certain volatility and thermal instability, and the weight loss of biochar after $ZnCl_2$ modification is the most stable. Yoon et al. [110] observed changes in the weight of paper mill sludge-derived biochar (PMSB) by TGA, and the results showed that its weight increased slightly (2.49 wt%) at temperatures ranging from 138 to 356 °C, and according to Sun [118] and Yoon et al. [119], this may be due to the oxidation of Fe(II) in magnetite to Fe(III). The weight gradually decreased as the temperature increased to 800 °C. The total loss of PMSB measured at 800 °C is about 10 wt%, which indicates that PMSB is mainly composed of inorganic compounds (i.e., iron and calcium minerals) except for a small amount of combustible carbon at high temperatures. From the TG image of (Figure 12) the hematite-modified biochar and the original pine biochar, it was observed that the thermal stability of the modified biochar is marginally higher than that of the original biochar [51]. The thermal properties of pristine pine cone biochar and Zn-modified biochar are shown in Figure 13. The pristine biochar had an exothermic peak at 330 and 480 °C, respectively, while only one exothermic peak was observed at 480 °C for the Zn-modified biochar. This is because the cellulose and hemicellulose of the biochar decomposed during the modification process, resulting in no peak at 330 °C for the modified biochar [116].



Figure 11. TG images of biogas residues, virgin biochar, and ZnCl₂-impregnated biochar [108]. Reprinted with permission from DongXia et al. (2016). Copyright 2016, Elsevier.

3.6. Other Characterization Methods

Raman spectroscopy is an analytical method to study the molecular structure by analyzing the scattering spectrum different from the incident light frequency to obtain information on molecular vibration and rotation. It has been applied to further understand the carbon structure of biochar [120,121]. Anste et al. [120] analyzed the Raman spectra of Miscanthus biochar (BC) and biochar modified by HNO₃ and H₂SO₄ (BC-N, BC-S, and BC-M). Figure 14 is a deconvoluted spectrum, the peak value of untreated biochar at 1563 cm⁻¹ is attributed to G-band aromatic respiration and graphite vibration. This peak is the primary band of BC and BC-S, which shows that there is a higher proportion of graphitic structures in BC and BC-S. In BC-M and BC-N samples, the peak changed and D' band appeared because of the secondary disordered carbon vibration, which is due to the formation of defects in graphite structure caused by strong acid treatment [122]. The movement of the G-band towards 1540 cm^{-1} may indicate an increase in formless carbon and smaller aromatic rings [123]. In a word, the carbon structure of biochar will be destroyed after strong acid treatment. Zhang et al. [124] observed that there are two main overlapping bands near 1350–1370 cm⁻¹ and 1580–1600 cm⁻¹ in the Raman spectrum of rice husk biochar (Figure 15), namely 'D' and 'G' bands, the former caused by in-plane vibrations of sp2-bonded carbon structures with structural imperfections, whereas the

reason for the latter is in-plane vibrations of sp2-bonded graphitic carbon structures, which is a perception that demonstrates a high proportion of amorphous carbon structures in biochar. In addition, the study by Xu et al. [125] showed that the pyrolysis temperature has a crucial effect on the degree of carbon structural order of biochar.



Figure 12. Thermogravimetric Analysis (TGA) of Pine Biochar (PB) and Hematite-Modified Biochar (HPB) [51]. Reprinted with permission from Shengsen Wang et al. (2014). Copyright 2014, Elsevier.



Figure 13. TG curves of original pine cone biochar and Zn-modified pine cone biochar [116]. Reprinted with permission from N. Van Vinh et al. (2015). Copyright 2015, Springer.



Figure 14. Deconvolution and peak fitting of Raman spectra belong to HNO_3 - H_2SO_4 treated biochar (BC-M). Peak distribution demonstrated for I_D (D band), IM (methylene/methyl band), I_G (G band), $I_{D'}$ (second disordered band), and I_C (carbonyl band) [120]. Reprinted with permission from Andrew Anstey et al. (2016). Copyright 2016, Elsevier.



Figure 15. The Raman spectroscopy of rice husk biochar [124]. Reprinted with permission from Kaikai Zhang et al. (2018). Copyright 2018, Elsevier.

X-ray absorption near-edge structure (XANES) can be utilized to describe the form of an element in biochar [126]. In the process of As adsorption, it can be used to explore the redox behavior and occurrence form of As on biochar [127]. For example, the ironmodified biochars prepared at different temperatures only have the oxidation of As (III) in the process of absorbing As, and the higher the pyrolysis temperature, the stronger the oxidation ability of As(III) to As(V). The results show that 20.2%~81.5% of As(III) is oxidized to As(V) [128]. Niazi et al. [129] used perilla leaves waste to prepare two kinds of biochars at 300 °C and 700 °C, respectively, and their XANES spectra showed that in the BC700-As(V) and BC300-As(V) adsorption experiments, up to 64% As(V) was reduced to As(III), while only a small amount of As(III) was oxidized to As(V) (37~39%) in the As (III) adsorption experiments. The result shows that the reduction of As(V) to As(III) is slightly larger than the oxidation of As(III) to As(V). Furthermore, Niazi et al. [130] also explored the solid phase morphology and redox transformation of As on Japanese oak wood biochar (OW-BC). This technique was also used to characterize biochar in the studies of Benis [45], Feng [131], Liu [132], and Munira et al. [133].

Confocal Micro X-ray fluorescence imaging (CMXRFI) can determine the distribution of various elements in biochar particles [31,134]. CMXRFI images show the distribution of three elements Ca, Fe, and As on the iron-modified biochar after reacting with As(III) and As(V) spiked systems for 24 h [128], Ca and Fe are scattered on the superficies and interior of modified biochar, and they are locally enriched. The image shows that As has no obvious relationship with Ca, but it is co-loaded with Fe on the biochar. Therefore, it can be concluded that the removal of As is mainly caused by Fe in the modified biochar. Feng et al. [131] prepared biochar from Populus adenopoda wood as biomass material (BM) and used this material to produce biochar (BC) at different temperatures (300 °C, 600 °C, and 900 °C) and modified it with FeCl₃ and FeSO₄, respectively. It can be clearly seen from Figure 16 that Fe, S, and Cl will diffuse into the biochar's pores, but simultaneously increase the pyrolysis temperature, and the aggregation of Fe, S, and Cl on the surface of the biochar also increases.



Figure 16. Elemental maps of FeCl₃BM (**a**), FeCl₃BC300 (**b**), FeCl₃BC600 (**c**), FeCl₃BC900 (**d**), FeSO₄BM (**e**), FeSO₄BC300 (**f**), FeSO₄BC600 (**g**), and FeSO₄BC900 (**h**) acquired utilizing confocal micro-X-ray fluorescence imaging (CMXRFI). Left passed on to right segment: Ca, Cl (S), Fe, and combined tri-color maps of these elements. The top part is the surface of the particle. The values in the bottom right corner are the maximum normalized intensities of the corresponding element [131]. Reprinted with permission from Yu Feng et al. (2019). Copyright 2019, Elsevier.

On the basis of several common biochar characterization methods, the application of these emerging technologies enables us to more intuitively understand the structure of biochar, the type, content, and distribution of elements contained in it, and other physicochemical properties. It provides more favorable conditions for exploring the adsorption mechanism of As on biochar. Therefore, it can be widely used in future research.

4. Influencing Factors of Arsenic Removal by Modified Biochar

4.1. Effect of Adsorbent Dosage

The dosage of biochar plays a significant role in As adsorption. The optimum dosage of biochar can adsorb As in water to the greatest extent and with high efficiency. The increase or decrease of the dosage may reduce the adsorption efficiency of biochar to As on biochar, while the optimal dose of biochar should be determined experimentally. Xu et al. [135] used paper mill sludge to prepare biochar (PMSB) in order to study its removal efficiency of Cu, Zn, and As in water. The research outcomes indicate that adding 0.1 g/L of biochar has the highest adsorption capacity of As, and the removal efficiency is 99.44%, while the addition amount of biochar increases to 0.3 g/L, the removal efficiency decreases slightly (97.96%) (Figure 17).



Figure 17. The effect of PMSB dosage on the removal efficiency (**a**) and adsorption capacity (**b**) of Cu, Zn, and As [135]. Reprinted with permission from Zhiyong Xu et al. (2021). Copyright 2021, Elsevier.

In another study, Sanyang et al. [136] revealed that the removal efficiency of As increased from 18.35 to 93% with the increased amount of hydrogel-biochar composite (HBC-RH) from 0.167 to 16.67 g/L. This is because the number of As adsorbable sites increases as the addition of biochar increases. When the addition amount was 10 g/L, the removal efficiency reached a balance. In addition, this study also found a significant decline in arsenic uptake per HBC-RH mass, which is because of the existence of abundant unsaturated sites on the biochar surface during the adsorption process. Lata et al. [47] also have similar findings, as the adsorbent dosage increased from 1 g/L to 2.5 g/L, the removal efficiency of As(V) increased continuously, but the removal efficiency becomes constant after the addition amount of adsorbent more than 2.5 g/L. Therefore, we can deduce that the adsorbent dose. After that, the effect of increasing the dosage on the removal of As is negligible, because the As in the solution is basically all adsorbed to the active sites of the biochar, and no other free As ions are adsorbed on the newly added biochar.

4.2. Effect of Solution pH

The pH of the solution plays an important role in the As adsorption of biochar. It not only affects the degree of ionization and morphogenesis of ions in an aqueous solution [47] but also affects their surface charge by affecting the protonation of functional groups on the biochar [137]. This is firmly connected with the zero-point potential of biochar (pH_{pzc}),

which refers to the pH of the solution when the net charge on the surface of biochar is zero. When the $pH > pH_{pzc}$, the charge of biochar is negative, which is conducive to the adsorption of cations such as Pb^{2+} and Cd^{2+} , when the pH < pH_{pzc}, the charge of biochar is positive, and it has a strong adsorption capacity for anions such as HAsO₄²⁻ and $HCrO_4^{-1}$ [31]. In addition, mechanisms such as ion exchange, electrostatic adsorption, etc. are also inseparable from pH [90]. Nham et al. [39] investigated the effect of solution pH on As adsorption efficiency by mixing 1.0 g Fe-BC with 100 mL of 10 mg/L As(V) solution with pH between 2.0 and 8.0 for 2 h. As shown in Figure 18, it is obvious that the removal efficiency of As(V) by the modified biochar is much higher than that of the primordial biochar, and simultaneously, the removal efficiency of As(V) in the acidic solution is higher than that in the alkaline solution which is because the OH^- in the alkaline solution will compete with the oxyanions of As for the active sites on the biochar. It is worth mentioning that both Fe-loaded biochar and iron oxide-based adsorbents are good adsorbents, but research on the former is preferred over the latter, because the amorphous form of iron oxide is easily transformed into well crystalline forms, resulting in a decrease in specific surface area and thus fewer adsorption sites. Due to the good crystalline form, the affinity for As is also reduced [138]. The maximum adsorption capacity of As(III) for both pristine biochar and Zn-modified biochar occurred under strongly acidic conditions (2–4), with adsorption capacities of 5.3 and 7.0 μ g/g, respectively, while increasing the pH from 4 to 12, the adsorption capacity gradually decreased. Vinh et al. [116] revealed that this is because in aqueous solutions, As(III) exists as a neutral or micro charged species that is not easily oxidized at alkaline pH. Therefore, its absorption is significantly lower at high pH.



Figure 18. Effect of solution pH on the removal of As(V) using Biochar and Fe-modified biochar [39]. Reprinted with permission from Nguyen Thi Nham et al. (2019). Copyright 2019, IOP Publishing.

While in several other studies, for example, the maximum adsorption quantity occurs at pH 3 when As(III) was adsorbed by Fe-Mn modified biochar (FMBC) with different pH values (Figure 19) [58], we can see that as the pH continued to increase, the adsorption capacity decreased [58]. The removal efficiency of hydrogel-biochar composite (HBC-RH) for As was significantly enhanced when the solution pH increased from 4 to 6, while the removal efficiency showed a decreasing trend when the pH continued to increase, this indicates that the optimum pH for arsenic removal by HBC-RH is 6, and the maximum adsorption capacity is 0.835 mg/g [136]. The effect of pH value on the composite of Fe-Mn-Ce and biochar is shown in Figure 20 [139]. The figure obviously shows that the adsorption effect of biochar on As(III) varies greatly at different pH values. When the pH value is 3, the adsorption effect is the best. As the pH value increases, the adsorption effect becomes worse. It is deduced that the removal efficiency of biochar at lower pH is higher than that

at higher pH, which is firmly connected with the surface charge of biochar. At lower pH, the protonation of biochar surface groups is favorable, which makes the biochar positively charged, thereby enhancing the adsorption capacity for As anions, while at high pH, the negatively charged surface of biochar would repel As anions and reduce its adsorption efficiency.



Figure 19. Effect of pH on adsorption of As(III) by FMBC [58]. Reprinted with permission from Lina Lin et al. (2017). Copyright 2017, Elsevier.



Figure 20. The effect of pH on adsorption by FMCBC₃ [139].

4.3. Effect of Reaction Temperature

The influencing factor of the reaction temperature is to observe the adsorption process and conduct thermodynamic research. Previous studies, such as Zhu et al, have shown that biochar adsorption of As is an endothermic process [107] reported that the adsorption heat difference (Δ H°) of As adsorption onto bismuth-impregnated biochar (BiBC500) exhibited a positive value, which indicated that the process was endothermic. Lin et al. [58] increased the reaction temperature from 288 K to 308 K and found that Fe-Mn-BC had enhanced adsorption capacity for As(III), and they also calculated the values of Δ H, Δ S, and Δ G, the positive value of Δ H illustrates that the adsorption of As(III) by Fe-Mn-BC is an endothermic reaction, which indicates that the higher temperature is favorable for the adsorption of As(III) adsorption. However, there are other studies with completely different results., Luo et al. [64] added pristine yak dung biochar and Fe-modified yak dung biochar to As(V) solutions (Ph = 5.0–6.0) at different temperatures (25 °C, 50 °C, and 80 °C), and the outcomes reveal that the effect of solution temperature on the adsorption of arsenic by biochar is negligible, and the removal efficiency has hardly changed. Lata et al. [47] observed the adsorption of As(V) on Fe-modified banana peel biochar (FeBPB) at three different temperatures (298 K, 308 K, and 318 K), and found that at 298 K, the removal efficiency was the highest, and the maximum adsorption quantity was 120.91 μ g/g. The higher the reaction temperature, the lower the removal efficiency of As(V), which reflects that the adsorption is exothermic. They hypothesized that because of the increased temperature, the biochar surface may have obtained higher energy, causing a large amount of adsorbed arsenate ions to escape into the solution.

4.4. Effect of Reaction Time

By studying the reaction time of arsenic adsorption by biochar, the adsorption rate of biochar and the time required for the adsorption process to reach equilibrium and its duration can be determined [136]. Nham et al. [39] set the reaction time from 0 to 180 min to study its effect on the adsorption of As(V) on biochar. During the time period from 0 to 60 min, the removal efficiency showed a significant upward trend, the adsorption rate was faster, and the adsorption reaches equilibrium in 90 min. Zhou et al. [40] established the adsorption equilibrium of As(V) on magnetic gelatin-modified chestnut shell biochar (MG-CSB) with reaction time ranging from 0 to 1440 min, as shown in Figure 21. In the first 3 min, the adsorption rate of As(V) was high, and 30% of the final adsorption occurred in this period time. The adsorption capacity increases with time until equilibrium is reached, and the equilibrium time was about 4 h with the adsorption capacity up to 28.7 mg/g. Meanwhile, the R² values of the pseudo-first-order model and pseudo-second-order model were 0.87 and 0.92, respectively, which indicated that the adsorption of As on MG-CSB was determined by chemisorption.



Figure 21. The pseudo-first-order and pseudo-second-order kinetics model fit of As(V) adsorption on MG-CSB (MG-CSB = 20 mg, As(V) concentration = 20 mg/L, pH = 7.3 ± 0.2 , t = 4 h, T = 298 K) [40]. Reprinted with permission from Zan Zhou et al. (2016). Copyright 2016, Elsevier.

As reported by Sanyang et al. [136], in the first 6 h, most of As has been adsorbed by HBC-RH, and the adsorption capacity reached 94.85%. After the reaction time reached 24 h, the adsorption capacity of As was 4.92%. During the period of adsorption equilibrium, biochar did not adsorb As owing to an enormous number of adsorption sites on the surface of biochar being occupied and the aggregation between the particles [31]. The total time to reach adsorption equilibrium was approximately 48 h. Lata et al. [38] added 0.25 g Fe-modified banana peel biochar (FeBPB) to 100 mL of As(V) solution with a concentration of 100 μ g/L, and the removal efficiency of As(V) increased continuously with the increase

of reaction time until all active sites were completely occupied, and the time is 2 h with the removal efficiency of As(V) up to 91.05%, and then maintain a relative balance of adsorption.

4.5. Influence of Ion Concentration

The As ion concentration reflects the As content in the solution. With higher ion concentration, more active sites can be used; therefore, the As adsorption capacity by biochar will increase [140]. Pristine biochar (PB) was modified by different amounts of FeCl₃, Fe, and Mn, and 0.08 g modified biochar was added to As(III) solutions with concentrations of 0.25, 0.5, 1.0, 2.0, 5.0, 10.0, and 50.0 mg/L, respectively, and it was found that the adsorption of PB no longer increased after 2 ppm of the As(III) concentration [140]. This was probably due to the earlier saturation of the active sites on PB than that of the modified biochar, which also shows that the modified biochar has greater potential to remove As than the unmodified biochar. Holding other conditions constant (1 g/L of HBC-RH dosage, contact time of 48 h, and pH of 6), Sanyang et al. [136] set the concentration range of As from 1 to 150 mg/L. The result shows the adsorption quantity of As on biochar rose steadily (from 0.423 to 27.56 mg/g) when the As concentration increased from 1 to 100 mg/L. However, when the concentration reaches 100 mg/L and greater than 100 mg/L, the adsorption process reaches an equilibrium state, and this further illustrates that adsorption sites on biochar are exhausted. The results of this study show that the removal efficiency of HBC-RH is better at a low arsenic concentration. Nham et al. [39] found that when the initial concentration of As(V) solution was 4 mg/L, the removal efficiencies of Fe-BC and BC for As(V) were 92.8 and 61.3%, respectively. Both Fe-BC and BC were less efficient in removing As(V) at higher initial arsenic concentrations, which was attributed to the limited adsorption sites on the biochar, most of which had been occupied by As(V). Moreover, the higher removal efficiency of Fe-BC than BC can be explained by the presence of Fe ions.

4.6. Influence of Co-Existing Ions

Due to the complexity of the ions contained in the water, the co-exist ions may affect the water phase equilibrium during the As adsorption process [45], therefore, it is important to study the effect of co-existing ions on the adsorption of As in water by biochar. Three types of adsorption usually occur between co-existing ions which are independent adsorption, cooperative adsorption, and competitive adsorption [141]. To study the effect of co-existing ions in solution on the adsorption of As(III) on modified biochar, Lin et al. [58] carried out batch adsorption experiments at room temperature using SO₄²⁻, NO₃⁻, and PO₄³⁻ with ionic strengths of 0.1 M, 0.01 M, and 0.001 M, respectively. The results show that the adsorption capacity of As at equilibrium is not related to the presence of SO_4^{2-} and NO_3^{-} , but increasing its concentration has a small positive effect on the removal efficiency of As(III). While the presence of PO_4^{3-} significantly reduces the adsorption capacity of As(III), the increased concentration resulted in enhanced adsorption capacity. This is attributed to the highly similar electronic configuration of As(III) and PO_4^{3-} [93,94]. PO_4^{3-} will form tetrahedral oxygen anion in an aqueous solution [142], and PO_4^{3-} competes with As(III) for adsorption sites on biochar. The order of the effect of competing anions on As(III) is $PO_4^{3-} > SO_4^{2-} > NO_3^{-}$. This is in accordance with the research result of Lata [47] and Zhang [59] et al., who selected PO_4^{3-} , Sb(OH)₆⁻, and $Cr_2O_7^{2-}$ as three typical oxygen anions with similar chemical properties to As(V), to evaluate their individual effects on As(V). Results showed that PO_4^{3-} has the strongest competition with As(V). Liu et al. [49] also had the same findings where PO4³⁻ had the greatest negative effect on As adsorption on biochar compared with Cl^- , NO_3^- , CO_3^{2-} , and SO_4^{2-} . In addition, it was found that these anions are easily trapped by adjacent hydroxyl or carboxyl groups present on the surface of the magnetic chitosan/biochar composite (MCB), which may alter the surface state of MCB and reduce the availability of binding sites. Figure 22 [94] shows the effect of carbonate, sulfate, fluoride, nitrate, and phosphate on the removal of As(V) from 20% Fe-modified biochar at pH 2.0, 6.0, and 10.0, which clearly illustrates the above conclusion.



Baig et al. [56] also found that in addition to the competitive adsorption mechanism, the existence of charge diffusion between PO_4^{3-} and As also affects the adsorption of As.

Figure 22. The effect of co-existing anions on the adsorption of As (20% FBC) [94]. Reprinted with permission from Ruozhu He et al. (2017). Copyright 2017, Elsevier.

The effect of co-existing cations on the As adsorption process should not be underestimated. Meng et al. [96] studied the effects of Na⁺, K⁺, Ca²⁺, and Mg²⁺ on the adsorption of As on biochar. The results are shown in Figure 23. No matter the cation concentration, Na⁺, and K⁺ both have little effect on the adsorption of As(V), while Ca²⁺ and Mg²⁺ promoted the adsorption of As(V) on biochar, and the adsorption capacity increases with the increase of Ca^{2+} and Mg^{2+} concentrations. They speculate that this is because the Ca^{2+} and Mg^{2+} ions compress the bilayer, allowing As(V) to more easily enter the inner pores, thereby enhancing the adsorption of arsenate. It is obvious from Figure 24 [62] that the addition of Cd (II) will greatly weaken the adsorption capacity of α -FeOOH@BC for As(III), and when the Cd(II) concentration was above 40 mg/L, the effect was more pronounced, suggesting that the addition of Cd(II) will have a competitive effect with As(III). Wu et al. [143] found that adding Cd(II) to As(III) solution would reduce the adsorption of As(III) on iron oxidemodified straw biochar, and the inhibition effect was the strongest when the concentration of Cd(II) was 20 mg/L (Figure 25). It is observed in Figure 26 that the adsorption of As(III) by biochar decreases and also increases with increasing the concentration of Cd(II), which shows that there is not only competition between ions, but also synergy.



Figure 23. Effects of different cations on the adsorption of 25 mg/L As(V) at 298 K [96]. Reprinted with permission from Fanqing Meng et al. (2017). Copyright 2017 American Chemical Society.







Figure 25. The effect of adding Cd(II) on the adsorption capacity of As(III) under different initial concentrations [143]. Reprinted with permission from Jizi Wu et al. (2018). Copyright 2018, Elsevier.



Figure 26. The effect of different initial concentrations of Cd(II) on the adsorption capacity of As(III) [143]. Reprinted with permission from Jizi Wu et al. (2018). Copyright 2018, Elsevier.

It is worth noting that compared with the monomeric form, the species in the polymer form would occupy more biochar surfaces and adsorption sites, thereby hindering the adsorption of As(V) through steric hindrance effects or by reducing the surface potential [144].

At present, most studies only use laboratory simulated arsenic-contaminated water but the actual arsenic-contaminated water is much complex than that of simulated water. Therefore, more practical arsenic-enriched water should be used to study the adsorption performance of modified biochar in the future.

5. Application of Modified Biochar in Arsenic Removal from Water

As a powerful and environmentally friendly new adsorbent, modified biochar has been widely used due to its larger specific surface area, richer pore structure, and surface functional groups than original biochar. It has also been gradually applied to improve the quality of various arsenic-contaminated waters, including groundwater, drinking water, industrial and agricultural wastewater, etc. Nham et al. [39] discussed the application of iron-modified biochar in actual arsenic-contaminated groundwater where the groundwater samples with an As(V) concentration of 97 μ g/L were tested, and the results showed that 1 kg of FeBC can treat 297 m³ and 165 m³ of arsenic-contaminated groundwater into clean water containing only 50 and 10 μ g/L As(V), respectively, in compliance with Vietnam's water supply and water supply regulations. In Tibet, geothermal resources are abundant, and arsenic in geothermal has high content, which is one of the typical harmful elements. The concentration can be as high as 3.56 mg/L [64] and if people drink water affected by geothermal water, it will cause different degrees of harm to health. To solve this problem, Luo et al. [64] used yak dung as raw material and modified it with $FeCl_2$ to remove arsenic in geothermal water. The original biochar can optimally remove 20% of As(V) under the same conditions, while Fe-BC removes 99.45% of As(V) under the same conditions. This demonstrates biochar prepared by pyrolysis of yak dung can be used to remove arsenic from geothermal water, and the modification greatly improves the arsenic removal efficiency of biochar. Similarly, Johansson et al. [145] also applied modified biochar to remove arsenic from coal-fired power generation wastewater. They used two different algae as raw materials and modified them with FeCl₃. The highest adsorption capacities of the two modified biochars for arsenic in wastewater were 62.5 mg/L and 80.7 mg/L, respectively.

However, most applications are still in the laboratory testing stage, and the real field applications are rarely reported. Cost-effectiveness is the main restricting factor in real field applications, therefore, a proper analysis of cost-effectiveness is the premise and basis for on-site application. There are many factors affecting the practical application of biochar, such as the characteristics of biochar, the physical and chemical properties of sewage, the natural environment, human management methods, and so on. Field-scale application requires equipment for large-scale production of biochar firstly and also needs to evaluate the technical feasibility of the practical application, which includes operating parameters, effects, and stability in the treatment process. In addition, how to recover or treat the used biochar is also a question worth discussing. In the future, research and analysis on these two aspects should be further discussed.

6. Mechanism of Arsenic Removal by Modified Biochar

At present, many mechanisms have been found to affect the process of arsenic adsorption by biochar, including surface adsorption, electrostatic attraction, ion exchange, precipitation, surface complexation, and redox reactions [61,140,146], and chemical interactions between metal ions and surface functional groups, which may be the formation of surface complexes between As(V) and modified biochar functional groups [53]. The above mechanism is shown in Figure 27. In addition, Table 3 summarizes the arsenic removal mechanism of partially modified biochar.



Figure 27. Principal removal mechanisms of As from water by modified biochar [81]. Reprinted with permission from KhaledZoroufchi Benis et al. (2020). Copyright 2020, Elsevier.

Surface adsorption means that arsenic ions enter the pores of modified biochar through self-diffusion to remove arsenic. Because the modified biochar has a larger specific surface area and richer pore structure than the original biochar, the modified biochar has a higher affinity for As, and more arsenic is retained in the pores [146]. For electrostatic adsorption, its effect is closely related to the pH value of the solution and the zero charge point of biochar [89]. According to Wang et al. [51], HAsO₄²⁻ is the main form of As(V), and some functional groups of biochar are protonated, so their charge is positive. In addition, according to the research of Chowdhury et al. [147], the zero charge point of iron oxide on the surface of hematite-modified pine biochar (HPB) is 7.5, which is positively charged, and the results show that HPB greatly improves the resistance to As adsorption capacity, because both iron particles and surface functional groups can be sites for adsorption of arsenic in aqueous solutions. The effect of ionic strength on the electrostatic interaction of ions cannot be ignored, which can affect the rate of ionic bond interaction. As the As species form a complex on the inner sphere surface, the adsorption of As increases or remains constant with the increase of ionic strength, but the adsorption may decrease with increasing ionic strength when the As species form a complex on the outer sphere surface [148]. During the complexation process, the D orbital of As interacts with the oxygen-containing functional groups on the biochar to form a polyatomic structure [149], the modification of the biochar increases the abundance of oxygen-containing functional groups on its surface, so the removal ability of As can be enhanced through complexation reaction. XRD and FT-IR can analyze the information of minerals contained in modified biochar and the changes of functional groups before and after arsenic adsorption, so they are often used to discuss this arsenic removal mechanism of modified biochar. For example, the FT-IR spectrum confirmed that Fe oxide was successfully loaded on water hyacinth, which was mainly magnetite (Fe₃O₄) detected by the XRD technique, and the hydroxyl peaks at 3417^{-1} , 3472^{-1} , 3554^{-1} , and 1319 cm⁻¹ on the FT-IR spectrum were significantly reduced, indicating that the As anion $(HAsO_4^{2-}/H_2AsO_4^{-})$ contacted the hydroxylase surface of Fe_3O_4 to form an inner sphere surface complex [59]. According to Li et al. [31], the complexation and electrostatic interaction are the main mechanisms for the adsorption of As on biochar, and functional groups are dominant in the complexation. Bakshi et al. [150] showed that ZVI was partially oxidized during the experiment to form

various FeOOH phases (goethite, lepidocrocite, and akaganeite) through XRD analysis. They infer that there is a co-precipitation behavior between Fe(III) and As(III) on zero-valent iron-biochar complexes, which can form various Fe(As)OOH phases, and since biochar is a semiconductor, it is favorable for the electron transfer of ZVI to O₂ or As(V) ions which can promote the precipitation reaction. However, precipitation is a secondary removal mechanism for arsenic compared to complexation and electrostatic interactions [31].

The existing forms of As have a considerable effect on its adsorption on biochar. Therefore, in addition to the arsenic removal mechanism discussed above, exploring the biochar-induced redox reaction is beneficial to better understand the As adsorption on biochar. The study by Wongrod et al. [151] confirmed that the oxidation of As(III) is caused by the biochar material itself, but this oxidation is only a small part, and arsenic is mainly adsorbed on KOH modified biochar in the form of As(III) (90–92%), and only 8–10% is adsorbed in the form of As(V). As we all know, As(III) is more toxic than As(V). Therefore, it is a promising repair strategy to oxidize As(III) to As(V) and then adsorb and remove it. The conversion of As(III) to As(V) can be promoted when there are redox-active substances (e.g., NO_3^- or FeO(OH)) on the surface of biochar or in the form of a metal oxide such as Fe and Mn [152].

Adsorbent	Arsenic Species	Sorption Capacity Q _{max} (mg/g)	pН	Best Isotherm Model	Best Kinetic Model	Proposed Sorption Mechanism	Reference
Fe(III)-modified Crop Straw biochars	As(V)	33.7 g/kg	5	Langmuir	/	Surface complexation	Pan et al. [153]
corn stem Biochar Impregnated with Fe-Mn Oxides	As(III)	8.80 mg/g	7	Freundlich	Pseudo-second-order	Surface adsorption, oxidation	Lin et al. [109]
ZnCl-activated biogas residue biochar	As(III)	27.67 mg/g	7	Freundlich	Pseudo-second-order	Ligand exchange, porous adsorption	Xia et al. [108]
FeCl ₃ treated corn straw biochar	As(V)	6.80 mg/g	6	Freundlich	Pseudo-second-order	Electrostatic attraction, precipitation	He et al. [94]
Hematite modified Pinus taeda biochar	As(V)	429 mg/kg	7	Langmuir	Elovich	Electrostatic attractions	Wang et al. [51]
Fe-impregnated hickory chips biochar	As(V)	2.16 mg/g	/	Temkin	/	Surface complexation	Hu et al. [44]
	As(III)	31. 4 mg/g	8		/	Surface complexation, interactions with FeOH and FeOH ²⁺ groups	Samsuri et al. [54]
Fe-coated empty fruit bunch biochar	As(V)	15.2 mg/g	5	Langmuir			
	As(III)	30.7 mg/g	9				
Fe-coated rice husk biochar	As(V)	16.0 mg/g	6				
Biochar-supported molybdenum-disulfide/iron-oxide	As(III)	30.9 mg/ g	4	Freundlich	Pseudo-second-order	Ligand exchange, the coexistence of SO4•– and •OH	Khan et al. [43]
Magnetic chitosan/biochar composite	As(V)	17.876 mg/ g	5	Langmuir	Pseudo-second-order	Electrostatic attraction and the increased adsorption sites that iron provided	Liu et al. [49]
KOH activated municipal solid wastes biochar	As(V)	30.98 mg/g	/	Langmuir	Pseudo-second-order	Surface complexation, π–π electron donor–acceptor interaction	Jin et al. [53]
α -FeOOH modified wheat straw biochar	As(III)	78.3 mg/g		Langmuir	Pseudo-second-order	Co-precipitation, ion exchange	Zhu et al. [62]
Fe ₃ O ₄ nanoparticle-covered Hybrid bamboo biochar	As(V)	868 mg/g	/	Langmuir	Pseudo-second-order	Electrostatic attraction, precipitation	Alchouron et al. [154]
Pinewood supported nZVI (nZVI/BC)	As(V)	124.5 mg/g	4.1	Freundlich	Pseudo-frst order	Surface complexation	Wang et al. [55]
Zero valentnano iron activated date palm biochar	As(V)	26.52 mg/g	2–6	Langmuir	Pseudo frst-order	Electrostatic interactions, surface complexation and diffusion	Ahmad et al. [155]
reO _x CaCO ₃ + paper mill sludge biochar	As(V)	23.1 mg/g	8.6	Langmuir	Pseudo-second-order	Electrostatic attraction, co-precipitation	Yoon et al. [110]
Fe ⁰ + red oak & switch grass biochar	As(III)	7.92–15.58 mg/g	7.0– 7.5	Langmuir	Pseudo second order	Surface adsorption, co-precipitation	Bakshi et al. [150]
Fe-composite Rice husk biochar	As(V)	0.760 mg/g	7	Freundlich	Pseudo second order	Precipitation, electrostatic attraction	Agrafioti et al. [156]

 Table 3. Modified biochar adsorbents mechanism for arsenic removal from water.

7. Summary and Prospect

This review demonstrates that biochar can be used as an effective adsorbent for As removal from water, and the modified biochar has a significantly improved removal rate of As in water, which is attributed to the enhanced physicochemical properties, especially the introduction of more functional groups since the complexation reaction is the most important mechanism of arsenic adsorption by modified biochar. Modified biochar shows increasing potential in removing arsenic from water. It is important to understand the structural changes and physicochemical properties of biochar when applying various characterization techniques. It was found that the process of As adsorption by modified biochar is affected by various factors such as solution pH, the reaction temperature and time, the As concentration, and the co-existing ions, etc., which should be evaluated in practical application.

Although modified biochar shows great potential in removing arsenic from water, there are still some issues that need further discussion and analysis:

- (1) Recently, the most frequently used technique for preparing biochar is pyrolysis technology. However, due to the time-consuming, and low efficiency of pyrolysis technology, and with the deepening of research, the requirements for adsorption materials are increasing. In order to obtain biochar with better performance, the research and use of emerging technologies such as hydrothermal carbonization and microwave can be strengthened.
- (2) The toxicity of trivalent methylated arsenic is far greater than that of inorganic arsenic, and there are few reports on this aspect.
- (3) Most of the research stays on the laboratory scale, and they are batch processing systems for a short time, while in the actual situation, they are continuous processing systems. Therefore, the practical application research of modified biochar in As removal should be investigated.
- (4) For field application, cost-effectiveness is a key constraint, and many commercial adsorbents have been widely used in actual water treatment. In order to increase the competitiveness of biochar, a cost analysis must be carried out. In addition, it is also necessary to increase the comparative study of arsenic removal efficiency with competitive adsorbents (e.g., activated carbon).
- (5) How to recycle or dispose of the used biochar to prevent secondary pollution of water and soil is also a question worthy of consideration.

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