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A Review of Biochar as a Stable Adsorbent for Removing Antibiotics from Wastewater

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Abstract
One of the most recent environmental concerns is the emergence of new pollutants, such as antibiotics, and increasing antimicrobial resistance in bacteria. Therefore, achieving effective methods for treating these pollutants is very important and considerable. Extensive studies have been conducted on antibiotic removal from water by carbon-based materials. Engineered biochar-based adsorbents and biochar composites can effectively increase the yield of antibiotics adsorption. Adsorbents based on biochars are made from various raw materials at different conditions. Also, physically and chemically modified biochars and their composites could be used. The structure and physicochemical properties of adsorbents and antibiotics and the environmental conditions affect the absorption of antibiotics by biochars. Research has shown that biochar has many advantages, including a wide variety of available raw materials, and they are cheap. Furthermore, it could be regenerated and reused by efficient management, which is the significant advantage of biochar-based adsorbents. Although biochar usage is a good choice for removing antibiotics from aqueous solutions, it is possible to improve its adsorption capacity with more studies to optimize the main parameters and new methods in its production and thus cause economic benefits.

Keywords: Biochar, Adsorption, Wastewater Treatment, Antibiotic, Composite.

1. Introduction
With the widespread use of antibiotics, problems related to their overuse have appeared (Gould, 2016; Abdi et al., 2022a). The existence of antimicrobial resistance[1] in bacteria led to the growth of recent pharmaceutical products. Several formations, such as WHO[2], have set one of their main aims to overcome this event (Jimenez et al., 2019). Fig. 1 shows the sources and routes of antibiotics entering the environment. Currently, antibiotics are known as emerging contaminants[3] (Lapworth et al., 2012; Golzadeh et al., 2020). Several ways have been tested to eliminate organic pollutants from the environment, which are grouped into two categories: (1) destructive approaches such as biological and chemical methods, and (2) non-destructive physical approaches (Homem and Santos, 2011; Asghar et al., 2019; Shahmirzaee et al., 2022). Adsorption as a non-destructive physical method is very popular, specifically in the elimination of antibiotics (Patel et al., 2019).

[1] Antimicrobial Resistance (AMR)
[2] World Health Organization (WHO)
[3] Emerging Contaminants (ECs)

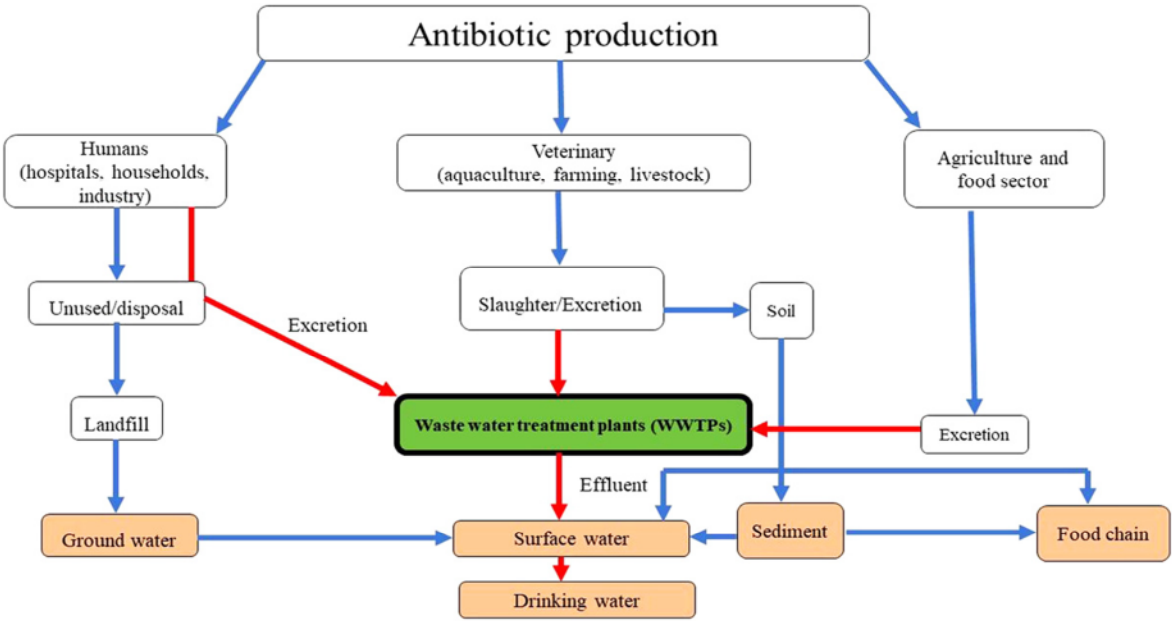

Fig. 1. Routes and sources of antibiotics in the environment (Adapted with permission from Ref. (Harrower et al., 2021))

The absorption procedure happens at the joint of liquid and solid phases (absorbent). The main origin of antibiotic contamination in the environment is the liquid phase like effluent (Homem and Santos, 2011; Abdi et al., 2022b; Abdi et al., 2014). Choosing a suitable adsorbent to remove pollutants from aqueous solutions is very important. The process of adsorption could be efficient and useful when the adsorbent matches the type of pollutants, so the chemical and physical properties (chemical structure, functional groups, sorption parameters like pore size and S_{BET}[1]) of the adsorbent must be known (Gupta et al., 2009; Firozjaee et al., 2020; Baghdadi et al., 2021; Abdi et al., 2021; Abdi et al., 2017).

The stability of the adsorbent is also considerable and important. Activated carbons[2] are useful for eliminating organic and inorganic pollutants (Gil Bravo et al., 2019; Mohan and Singh, 2005; Jeirani et al., 2017). However, by considering the commercial aspect along with the possibility of extensive modification, biochar (BC)-based adsorbents have attracted a lot of attention in recent years (Mohan et al., 2014; Tytłak et al., 2015; Sulyman et al., 2017; Braghiroli et al., 2018, Inyang et al., 2016; Mahmoodi et al., 2019b; Mahmoodi et al., 2019a)

2. Antibiotics

Mass production of antibiotics to fight microbiological (mainly bacterial) infections began in the twenty-first century. Because the isolation of natural antibiotic molecules was a difficult process, most of the used antibiotics were semi-synthetic, with few fully synthetic compounds (Ribeiro Da Cunha et al., 2019). As a result, the bacterial strains were exposed to the selective pressure of antibiotics. Such pressures from antibiotics affect the human microbiome and microbial communities in water and soil-related ecosystems. Considering the high importance of complex and diverse environmental microbiomes in soil, water, and plants (East, 2013; Doty, 2017), researchers pointed out that increasing the presence of antibiotics in the environment can intensify selection pressure and thus help attract resistance factors (Crofts et al., 2017).

Scientists are trying to overcome such a threatening issue by investigating the occurrence, sources, and routes of contamination, the fate of synthetic antibiotics, and derived residues in the environment (Zhou et al., 2022; Mahmoodi et al., 2019a; Abdi et al., 2022b).

3. Adsorption process by BCs

The process of adsorption relies on the interaction of the adsorbed material with the adsorbent. Different exchanges play important roles in the absorption of antibiotics on biochar; Electrostatic interactions, hydrophobic interactions, and π-π interactions are remarkable. Moreover, complexing the surface or filling the pores with absorbent material could happen (Tong et al., 2019).

Possible interactions in the adsorption of BC-antibiotics are illustrated in Fig. 2; indeed, none of these mechanisms will happen in each of the BC-antibiotics process, due to the physicochemical properties of the

[1] Specific surface area
[2] Activated Carbons (ACs)

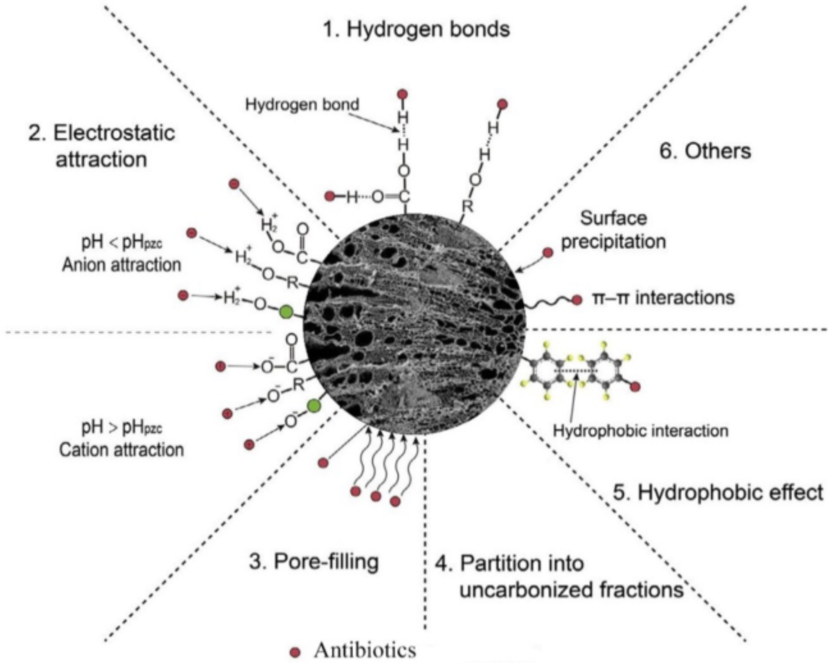

Fig. 2. Possible mechanisms during the adsorption of antibiotics (Adapted with permission from Ref. (Tan et al., 2015))

adsorbate and adsorbent. Several elements could be impacted by the adsorption procedure and its capacity. These factors include:

1. Physical and chemical properties of the adsorbent (pore structure, S_{BET}, presence of functional groups)
2. The kind and essence of the adsorbent (pKa, presence of functional groups, polarity, solubility, molecular size)
3. The tendency of the adsorbent for the adsorbent and the situations of mechanism (solution pH and ionic strength, temperature) (Ahmed et al., 2015; Premarathna et al., 2019b).

3.1. BC-based adsorbents for antibiotics

There are different methods to improve the structure and efficiency of biochar-based adsorbents. Based on the mechanism and modification of the synthesis, the obtained substances could be classified as pure/original BCs and engineered BCs, which allows the second group to be divided into modified biochars and biochar composites (Krasucka et al., 2021).

3.1.1. Pure BCs

Pure biochars are made through slow pyrolysis of biomass under a maximum temperature of 700 °C, in the presence or absence of oxygen (less than 2%) (Ahmed et al., 2015; Major et al., 2009; Manyà, 2012). Table 1 shows the results of some studies that have been investigated so far for the removal of antibiotics by different kinds of pure biochars.

3.1.2. Engineered biochars

Pure BC-based adsorbents showed an unacceptable capacity for the adsorption of different antibiotics. This issue is related to the lack of interaction between the adsorbent and medicine due to the aromaticity of the biochar, and polarity, with or without the needed/unneeded surface functional groups. Poor absorption, related to filling the pores, is caused by low porosity factors such as S_{BET}, pore volume[1], and limited diameter of the pores compared to the size of the antibiotic. It is essential to modify and improve the structure of biochars for increasing the adsorption of ECs such as antibiotics. So it can be classified into the physical and chemical approaches (Krasucka et al., 2021). Fig. 3 shows different modifications of engineered biochars for removing pollutants from the environment.

Physical modification

This approach includes activation by gas, ball milling, and microwave pyrolysis. The first two methods belong to the post-synthesis methods, in which modification is done on previously synthesized biochars. gas or steam activation and also ball milling is related to the post-synthesis approaches. The third modification is using microwaves for heating during the pyrolysis and making modified biochars (Wang et al., 2017; Foong et al., 2020).

[1] Pore Volume (PV)

Table 1. The capacity of antibiotic adsorption on different kinds of pure biochars under several conditions (Adapted with permission from Ref. (Jang and Kan, 2019b; Liu et al., 2016; Zhang et al., 2018b; Xie et al., 2014; Dai et al., 2020; Shang et al., 2016; Chen et al., 2018; Li et al., 2019))

Raw materials of BC	Pyrolysis conditions temp. (time), gas	S_{BET} (m^2/g)	Antibiotic	Adsorption conditions	Q_{max} (mg/g)
Alfalfa Medicago sativa L.	500 °c (0.5 h), N_2	31.1	Tetracycline (TC)	t= 5 d, pH= 5, T= 25°C, BC=0.1 g/L, C_{ant}= 10-100 mg/L	372.31
Bull manure	600 °C, N_2	250.0	Lincomycin (LIN)	t= 48 h, T= 25°C, BC= 1 g/L, C_{ant}= 1 mg/L	0.30
Sugarcane bagasse	500 °C (24 h), oxygen-limited	248.1	Chlortetracycline (CTC)	t= 24 h, pH= 5, T= 25°C, BC= 10g/L, C_{ant}= 200 mg/L	16.96
Red pine	400 °C (2 h), aerobic pyrolysis 500°C (2 h), aerobic pyrolysis	101.0 28.0	Sulfamethoxazole (SMX) Sulfapyridine (SPY)	t = 72 h, pH = 6, T = RT, BC = 10–15 mg/L	1.9 SMX 1.5 SPY 22 SMX 21.2 SPY
Waste Auricularia auricula dregs	300 °C (2 h), N_2	2.6	Tetracycline (TC)	t = 12 h, T = RT, BC = 0.8–4 g/L, C_{ant} = 10–25 mg/L	7.22
Astragalus mongholicus	200 °C (5 h), oxygen-limited	–	Ciprofloxacin (CIP)	t = 12 h, T = 25 °C, BC = 2 g/L, C_{ant} = 100 mg/L	5
Rice straw	400 °C (2 h), oxygen-limited	6.7	Tetracycline (TC)	t = 72 h, pH = 5, T = 25 °C, BC = 3 g/L, C_{ant} = 32 mg /L	8.3
Pinewood	600 °C (3 h), N_2	337.0	Tetracycline (TC)	t = 48 h, T = 25 °C, BC = 0.08–0.5 g/L, C_{ant} = 6–48 mg/L	5.53

S_{BET}: the specific surface area determined from N_2 sorption measurements according to the BET equation, t: adsorption time, pH: adsorption pH, T: adsorption temperature, BC: adsorbent dose, C_{ant}: initial antibiotic concentration, Q_{max}: the maximum adsorption capacity.

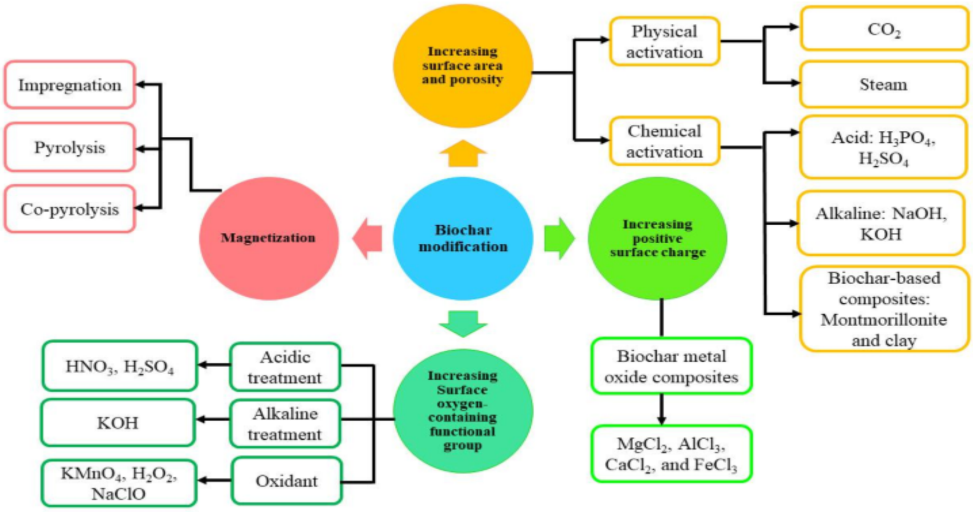

Fig. 3. Various modifications into the biochar (Adapted with permission from Ref. (Goswami et al., 2022))

Chemical modification

Post-synthesis chemical modifications such as oxidizing or reducing properties can be done on the pure biochar, and then it could be dried in simple ways (Wei et al., 2018) or advanced drying in the microwave (Ge et al.) 2020). In the pre-synthesis, raw material is chemically modified and then pyrolyzed (Wei et al., 2018). The difference between physical and chemical modifications is the major aim of physical modification is improving the porosity of biochar, while the main purpose of chemical modification is changing the essence of biochar, mostly causing the development in the surface oxygen functional groups (Sizmur et al., 2017). Table 2 shows the adsorption of antibiotics by using modified biochars.

3.1.3. BC composites

The most complicated category of BCs is composites. Based on the IUPAC[1] category, a composite is a multi-component material that includes various (non-gas) phases with at least one kind of continuous phase domain; if one of the phases has nanoparticle dimensions, it is called nanocomposite (Nič et al., 2009). Fig. 4 shows the impact of the commonly used additions on the characteristics of BC composites.

Clay biochar composites

Clay minerals such as montmorillonite and palygorskite have a high potential for eliminating different pollutants, due to their layered structure, high ion exchange capacity, and S_{BET} (Awad et al., 2019; Foroutan et al., 2019). Furthermore, they are attainable and economical. Although, the efficiency of clay minerals is reduced due to their small particles (Yao et al., 2014).

Carbon biochar composites

Biochar compounds with carbon materials are also used, such as graphene, graphene oxide, carbon nanotubes, and reduced graphene oxide (Sarkar et al., 2018; Chuanyu and Yu, 2015; Tang et al., 2015; Sizmur et al., 2017). Increasing the S_{BET}, mechanical constancy and thermal resistance of a composite can be caused by adding carbon materials to biochar (Tang et al., 2015; Zhang et al., 2018a; Ashiq et al., 2019; Premarathna et al., 2019a; Mukhopadhyay et al., 2020).

Carbon biochar composites are used to eliminate different pollutants such as heavy metals, dyes, pesticides, and drugs from water (Tang et al., 2015; Huang et al., 2017a; Zhang et al., 2018c). Several investigations have been done on the use of composite materials like graphene oxide (Huang et al., 2017a) and carbon nanotubes (Inyang et al., 2015) for antibiotics removal.

Metal biochar composites

Metals (Fe^0, Ag^0, Cu^0, Ni^0) and their compounds, oxides (MgO, MnO, Al_2O_3, Fe_2O_3, CaO), and hydroxides (AlOOH, $Mg(OH)_2$) have been used in the synthesis of biochar composites (Cheng and Li, 2018). Modification of biochar with metal oxides or hydroxides cause the enhancement of the porosity and change the physical and chemical characteristic of the composite, especially, changing the surface charge from negative (properties of biochars) to positive (properties of metal oxides). These types of composites can be used to adsorb negatively charged compounds from water, especially oxyanions (AsO_4^{3-}, AsO_3^{3-}, CrO_4^{2-}, NO_3^-, and PO_4^{3-}) that are harmful to health and the environment. These anions have shown a lack of tendency for pure biochars (Cho et al., 2019).

[1] The International Union of Pure and Applied Chemistry (IUPAC)

Table 2. The adsorption of antibiotics by using modified BCs (Adapted with permission from Ref. (Huang et al., 2017b; Rajapaksha et al., 2014; Liu et al., 2012; Tan et al., 2019; Jang et al., 2018; Fan et al., 2010; Gómez-Pacheco et al., 2012; Jang and Kan, 2019a))

Raw materials of BC	Pyrolysis conditions: Temp., Time, Gas	Sorbents/Modified sorbents	S_{BET} (m^2/g)	Antibiotic	Adsorption condition	Q_{max} (mg/g)
Poplar sawdust	300 °C (6 h) 500 °C (6 h) 300 °C (6 h)	Pristine BC Post-synthesis by stirring (5 h, 65°C) in 2 M KOH	- 1.6 12.3 106.8 111.4 337.8	Tetracycline (TC)	t= 72 h, T= 25°C, C_{ant}= 10-90 mg/L	4.3 21.17 7.37 4.97 11.63 7.13
Tea waste	700 °C, (2 h), oxygen-limited	Pristine BC Steam-activated BC (5 mL/min, 45 min, 700 °C)	342.2 576.1	Sulfamethazine (SMT)	t= 72 h, pH= 3, T= 25°C, BC= 1 g/L, C_{ant}= 2.5-50 mg/L	7.12 33.81
Rice-husk	500-550 °C, oxygen-limited	Pristine BC Post-synthesis with acid MeOH	51.7 66.0	Tetracycline (TC)	t= 312 h, T= 20°C, BC= 1g/L, C_{ant}= 100 mg/L.	81 95
Rape stalk	300 °C (4 h) N_2 450 °C (4 h) N_2 600 °C (4 h) N_2	Pristine BC Post-synthesis by stirring (24 h, 25 °C) in 30% H_2O_2	3.9 1.8 6.8 4.2 112.4 117.1	Tetracycline (TC)	t = 48 d, T = 25 °C, BC = 0.1 g/L C_{ant} = 1–15 mg/L	35.9 34.0 26.33 32.83 32.0 42.45
Pinus taeda	300 °C, N_2	Pristine BC Post-synthesis by mixing BC with 4 M NaOH solution for 2 h and carbonized (800 °C, 2 h)	1.4 959.9	Tetracycline (TC) Sulfamethoxazole (SMX)	t = 3 d, pH = 6, T = 20 °C, BC = 0.1 g/L, C_{ant} = 10–100 mg/L t = 5 d, pH = 5, T = 20 °C, BC = 0.1 g/, C_{ant} = 10–100 mg/L	29.42 274.81 58.91 437.36
Bamboo	450 °C	Pristine BC 10% H_2SO_4 10% KOH Post-synthesis by stirring (6 h, 60 °C)	< 1 < 1 < 1	Chloramphenicol (CAP)	t = 0.5 h, T = 25 °C, BC = 8 g/L, C_{ant} = 20 mg/L	0.6 1.5 2.5
Treatment plant sludge	700 °C	Pristine BC Pre-synthesis modif. impregantion sludge in NaOH (50 g/100 g w/w)	31.4 134.0	Tetracycline (TC)	t = 8d, T = 25 °C	302 1248
Alfalfa hays	300 °C, N_2	Pristine BC Pristine BC carbonized at 800 °C for 2 h Post-synthesis modif. by mixing BC with 4 M NaOH solution for 2 h and carbonizated (800 °C, 2 h)	0.7 50.6 796.5	Tetracycline (TC)	t = 5 d, pH = 5, T = 20 °C, BC = 0.1 g/L C_{ant} = 10–100 mg/L	30.70 55.62 302.37

S_{BET}: the specific surface area determined from N_2 sorption measurements according to the BET equation, t: adsorption time, pH: adsorption pH, T: adsorption temperature, BC: adsorbent dose, C_{ant}: initial antibiotic concentration, Q_{max}: the maximum adsorption capacity.

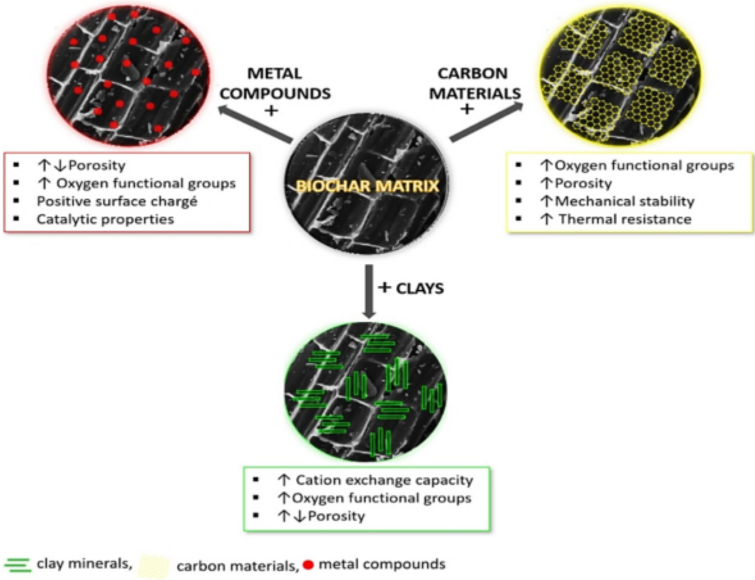

Fig. 4. Effects of the metal compounds, carbon materials, and clay minerals on the properties of BC composites (Adapted with permission from Ref. (Krasucka et al., 2021))

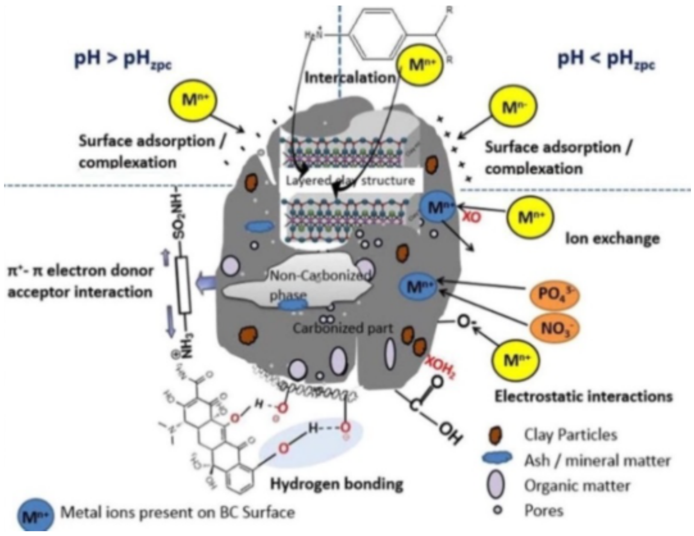

Fig. 5. The major mechanisms involved in the adsorption of contaminants on modified BC with metal ions present on BC surface (Adapted with permission from Ref. (Premarathna et al., 2019b))

Fig. 5 shows the adsorption mechanisms of inorganic and organic compounds in the presence of metal ion exchanges.

4. Holistic evaluation

According to the previous studies, biochar materials have a high economic potential for the antibiotics elimination. However, it should be considered that this subject matter is new. So, it is very essential for several research studies to be done to improve the knowledge in this field. More extensive research in this field increases the efficiency of these materials and manages the existing challenges. Some of these challenges are: having enough knowledge about the procedure of connection between the antibiotic and the adsorbent used, synthesis of suitable biochar with the highest efficiency, study on different types of primary and modified biochars, economic management of biochars, and considering their production and reuse costs, and environmental expense estimation (Krasucka et al., 2021).

4.1. Management of the used BC adsorbents

Used biochar adsorbents make challenges that must be managed well. Relying on the price of materials and the kinds of contamination, used absorbents are recycled, regenerated, or turned into waste (Reddy et al., 2017; Gómez-Pastora et al., 2014). Contaminants could be removed by the adsorbent, but this procedure is usually reversible, specifically in physical adsorption. Therefore, throwing away the absorbents that are contaminated with pollutants will be expensive and additionally, cause environmental pollution in the soil, groundwater, and surface water at their landfills (Reddy et al., 2017). Burning the discharged absorbents leads to the release of toxicant gases and ash with dangerous compounds and it is also very expensive (Bhagawan et al., 2015).

A new and optimal solution for the reuse of biochar is based on catalytic oxidation (such as the Fenton reaction), which leads to the degradation of the adsorbent. The efficiency of all existing methods depends on many factors, including the type of adsorbent and the interaction between the adsorbent and the adsorbed material (Reddy et al., 2017; Gómez-Pastora et al., 2014; Bhagawan et al., 2015; Dai et al., 2019; Ani et al., 2020).

Regeneration by chemicals and high temperatures affects the properties of biochar and changes the structure and porosity of the adsorbent, which can cause a decrease in their efficiency, for example, a change in absorption capacity (Deng et al., 2018). This is especially true for the regeneration of engineered biochars, which is mainly characterized by the existence of functional groups or some additives such as catalytic compounds in composites. So, depending on the kind of BC-adsorbate system, it is very vital to have a case-by-case approach. Reusing adsorbent with a bound adsorbate in other different places of life could be considered as an alternative to using the spent biochar. BC-based adsorbents used to remove phosphate ions could be utilized as soil fertilizers (Li et al., 2016; Cho et al., 2019; Wang et al., 2015; Li et al., 2018; Wang et al., 2019; Iris et al., 2019; Yang et al., 2016; Ani et al., 2020; Yao et al., 2013).

Biochar with adsorbed trace metals could be used as feed additives or catalysts (Reddy et al., 2017). Previous studies illustrated that biochars can be used in energy such as a solid fuel (Waqas et al., 2018; Abdullah and Wu, 2009), or as an additive in biogas production (Dudek et al., 2019; Wambugu et al., 2019). Therefore, it is possible to use the spent BCs-based adsorbent for this goal.

4.2. Environmental and economic advantages of BCs

The consumption of biochar as a pollutant adsorbent has brought a positive economic status. BC is a cheaper alternative to AC ($350-1200 per ton of BC versus $1100-1700 per ton of AC) (Thompson et al., 2016). The price of BCs relies on the cost of raw materials, pyrolysis, transport, and keeping the BCs (Shackley et al., 2011). The suitability of BCs in the economical aspect is very vital. Some data reports that the whole income from biochar sales was $8012 per year. By selecting new, cheap materials and optimal production technologies, the price of BCs could be decreased (Oni et al., 2019). Therefore, it is beneficial for the economy and the environment to use various kinds of waste and manure in the preparation of biochar (Oni et al., 2019; Ahmed et al., 2016).

Finally, there are no doubt those BCs, as adsorbents for removing pollutants in water and wastewater, have positive impacts on the environment. It is necessary to ensure the harmlessness and reusability of the adsorbent. For this reason, the use of carbons for water treatment, relying on the application, must have the necessary standards, like European EN 12915 1:2009 (products used for water treatment intended for human consumption) or EN 15799:2010 (products used for the treatment of swimming pool water). According to the new procedure of using BCs for water treatment, so far, no law has been established for their commercial use. Increasing the knowledge in the field of BCs increases efficiency and economic importance (Krasucka et al., 2021).

5. Conclusions

Environmental pollution with antibiotics have caused harmful and dangerous effects on humans, organisms, and the environment. The annual consumption of antibiotics is increasing sharply. This causes an increase in environmental pollution. As a result, studying and designing the most efficient approaches to eliminate this emerging pollution has garnered great attention. The outcomes illustrated that engineered biochar, as adsorbents, could be efficient for the removal of antibiotics. Biochar-based adsorbents can be effective for the removal of antibiotics by degradation. The yield of the absorption depends on the type of composition and the absorption conditions and the characteristics of the adsorbent and the contaminant. All these factors affect possible absorption processes.

The connection between the antibiotic with the BC adsorbent surface depends on the functional groups, the degree of BC graphitization, and pH_{pzc}. Recognizing the connecting mechanisms for different antibiotics plays a vital role in future research.

With sufficient knowledge and information, it will be possible to select an efficient and appropriate adsorbent to adsorb the desired antibiotic and to produce or optimize the required materials with a high yield of removal. Finally, the efficiency of biochar in removing emerging pollutants on a real scale is also an important requirement.

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