



# Biochar-mediated removal of pharmaceutical compounds from aqueous matrices via adsorption

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## Abstract

Pharmaceutical is one of the noteworthy classes of emerging contaminants. These biologically active compounds pose a range of deleterious impacts on human health and the environment. This is attributed to their refractory behavior, poor biodegradability, and pseudopersistent nature. Their large-scale production by pharmaceutical industries and subsequent widespread utilization in hospitals, community health centers, and veterinary facilities, among others, have significantly increased the occurrence of pharmaceutical residues in various environmental compartments. Several technologies are currently being evaluated to eliminate pharmaceutical compounds (PCs) from aqueous environments. Among them, adsorption appears as the most viable treatment option because of its operational simplicity and low cost. Intensive research and development efforts are, therefore, currently underway to develop inexpensive adsorbents for the effective abatement of PCs. Although numerous adsorbents have been investigated for the removal of PCs in recent years, biochar-based adsorbents have garnered tremendous scientific attention to eliminate PCs from aqueous matrices because of their decent specific surface area, tunable surface chemistry, scalable production, and environmentally benign nature. This review, therefore, attempts to provide an overview of the latest progress in the application of biochar for the removal of PCs from wastewater. Additionally, the fundamental knowledge gaps in the domain knowledge are identified and novel strategic research guidelines are laid out to make further advances in this promising approach towards sustainable development.

**Keywords** Pharmaceuticals · Adsorption · Adsorbents · Biochar · Wastewater treatment

## Abbreviations

ACE	Acetaminophen	CPX	Cephalexin
AMX	Amoxicillin	DFC	Diclofenac
AOP	Advanced oxidation process	FTIR	Fourier transform infrared spectroscopy
ASP	Activated sludge process	IBP	Ibuprofen
CAF	Caffeine	IPD	Intra-particle diffusion
CBZ	Carbamazepine	KETO	Ketoprofen
CFX	Ciprofloxacin	LEV	Levofloxacin
CNT	Carbon nanotubes	MMT	Montmorillonite
COD	Chemical oxygen demand	MSW	Municipal solid waste
		NF	Nanofiltration
		NPX	Naproxen
		NSAID	Non-steroidal anti-inflammatory drugs
		OFL	Ofloxacin
		PCs	Pharmaceutical compounds
		PFO	Pseudo first order
		PSO	Pseudo second order
		RO	Reverse osmosis
		RP	Redlich–Peterson
		SA	Salicylic acid
		SSA	Specific surface area
		SD	Sodium diclofenac

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SMX	Sulfamethoxazole
TC	Tetracycline
TCS	Triclosan
UF	Ultrafiltration
WWTP	Wastewater treatment plant

## Introduction

The frequent detection of xenobiotics in the ambient environment is a rising concern, among urban local bodies and health experts, because of their persistent nature and higher half-life. In the past few decades, rapid advancement in industrialization and urbanization has led to widespread exploitation of primary resources [1]. Several processing steps are involved during the manufacturing of consumer goods and products that release an enormous quantity of waste in different phases (solid, liquid, or gaseous), all of which are generally hazardous to the environment [2, 3]. According to the World Health Organization, approximately 15% of hospital waste is infectious and is considered toxic as well as hazardous. Traditionally, wastewater is often considered as one of the popular sinks for pharmaceutical compounds (PCs) [4–6], personal care products [7], pesticides [8], endocrine-disrupting compounds [9, 10], and other similar compounds. The ubiquitous nature of PCs can be attributed to their persistent release into the environment in contrast to their relatively slow transformation rate. Various pharmaceutical manufacturing industries produce wastewater, comprising a wide array of PCs, as well as with high chemical oxygen demand (COD), and sometimes even high salinity levels [11]. In particular, the minimum concentration of PCs in the aquatic environment prevails on the order of magnitude of  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  [12–16]. PCs are chemically stable compounds that are unregulated, and are often referred to as micropollutants, as their fate and transport are highly complex. Moreover, their physicochemical properties determine the extent and severity of PC contamination in a particular media, such as soil, water, and air.

During 2000–2015, the usage of antibacterial medications rose by up to 65% globally. The worldwide consumption of pharmaceuticals is predicted to increase by 200% by 2030 from the 42 billion defined daily doses in 2015 [17]. For instance, during the recent COVID-19 pandemic,

an unprecedented rise in the usage of drugs and medications was observed [18]. Generally, PCs tend to encroach on the host environment, such as aqueous media, viz., surface water, groundwater, cryosphere, and wastewater. Eventually, PCs transform into various intermediates via interactions with both biotic and abiotic components of the environment, depending upon their reactivity and sensitivity. As a result, the aquatic environment suffers serious threats such as the generation of resistant microbial species.

Generally, pharmaceutical substances in aqueous matrices originate from human consumption via the excretion of both metabolized and unmetabolized drugs, as well as the incorrect disposal of unused medicines, usually by flushing down the toilet/sink or by discarding them into waste bins destined for landfills. As conventional wastewater treatment technologies are largely ineffective at eliminating PCs, the effluents of wastewater treatment plants (WWTPs) often contain significantly high levels of antibiotics, analgesics, tranquilizers, antiepileptic, stimulant drugs,  $\beta$ -blockers, antimicrobials, antiseptics, and non-steroidal anti-inflammatory drugs (NSAID) [19]. For example, PCs, such as acetaminophen (ACE), ibuprofen (IBP), ketoprofen (KETO), naproxen (NPX), sulfamethoxazole (SMX), and diclofenac (DFC), fall under the category of NSAID or analgesics and pose detrimental effects on different environmental matrices. Similarly, other PCs belong to different classes of drugs and show unwanted environmental effects, as listed in Table 1. The recalcitrant nature of PCs in aqueous matrices often leads to the development of persistent genes in microorganisms. When pharmaceutical drugs are detected in any environmental compartment, they are either present in their original form or as metabolites, which are even more harmful than the former. As shown in Fig. 1, the fate and transport of PCs, their metabolites and transformed products follow interdependent complex pathways, and the major sources of contamination include pharmaceutical industries, hospital residues, farm livestock, unused medicines or drug disposal from different households [19]. The higher level of PCs in the environment can cause chronic diseases, cancer, antibiotic resistance, metabolic issues, endocrine disruptions, and may even unbalance the microflora [20]. The aquatic ecosystem in particular is deranged by lowering of fertility, accumulation of PCs within tissues, damaging fish spawning, etc. [21].

**Table 1** Summary of a wide array of pharmaceutical compounds (PCs), their use, and environmental effects in aqueous matrices

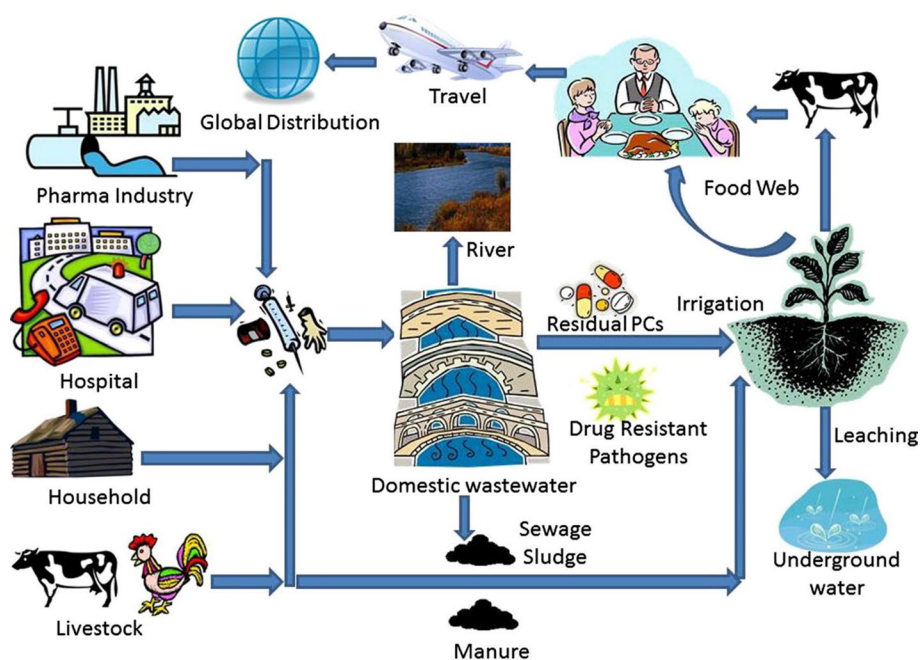
Pharmaceutical class	PCs	Therapeutical use	Adverse effects when left untreated in the environment	References
Analgesic	Ibuprofen (IBP)	NSAID and analgesic drug	Endocrine-disruption in humans and other organisms, leading to damage in the neurological system Deterioration of groundwater and freshwater quality	[22–25]
	Ketoprofen (KETO) Naproxen (NPX)	NSAID and analgesic drug	Accumulation in agricultural soil Continuous exposure to aquatic organisms in the range of nanogram to microgram induces long-term detrimental effects	[26]
	Diclofenac (DFC)	NSAID	Noxious effects on many organisms	[27]
	Acetaminophen (ACE)	Antipyretic analgesic	Severe toxicity to aquatic life due to the release of various metabolites Results in the development of antibiotic-resistant bacteria	[23, 28, 29]
Antibiotic	Ciprofloxacin (CFX)	Synthetic antibiotic	Negatively affects surface water and groundwater quality	[30, 31]
	Sulfamethoxazole (SMX)	Human and veterinary antibiotic	Bioaccumulation in aquatic organisms Induces antibiotic-resistant genes in various organisms	[32, 33]
	Chlortetracycline (CTC)	Veterinary antibiotic	Adverse effects on various aquatic organisms like histological alteration in gills of fish by pro-oxidative activity Development of antibiotic resistance in various bacteria	[34]
Antimicrobial	Levofloxacin (LEV)	Bacterial antibiotic	Antibiotic resistance in humans and animals	[35, 36]
	Triclosan (TCS)	Antimicrobial ingredient	Endocrine disruption, development of tumors, alterations in thyroid hormone metabolism in humans	[37, 38]
Anticonvulsant	Carbamazepine (CBZ)	Antiepileptic	Bioaccumulation and toxic effects due to its negligible degradation	[39, 40]
Stimulant drug	Caffeine (CAF)	Stimulant drug	Negative impacts on microalgae, corals, bivalves, sponges, marine worms, fish and other aquatic species	[41, 42]
Antihypertensive	Propranolol (PRO) Atenolol (ATO) Metoprolol (MTP)	Beta-blockers	Severe bioaccumulation in aquatic organisms due to limited immobilization in natural soils or sediments Disruption in the testosterone level of male organisms	[43]

The key efforts towards limiting the negative impacts of PCs are focused on their accurate quantification, identification, control, and eradication from aqueous systems. Numerous sophisticated analytical techniques, such as ultrapure liquid chromatography/mass spectrometry, gas chromatography/mass spectrometry, and liquid chromatography/mass spectrometry, have simplified quantification and established the occurrence of PCs within the range of  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  [44]. Typically, the removal of emerging contaminants is ineffective due to the intrinsic design limitations of WWTPs [6]. The conventional treatment processes, namely, chemical, biological, and physical processes, are insufficient to degrade PCs. To that end, various researchers have shown efficient abatement of PCs through high pressure reverse osmosis (RO) [45], nanofiltration (NF) [45], adsorption,

advanced oxidation, and electrodialysis, among others [20, 46]. In particular, adsorption-based separation is technoeconomically feasible for removal of PCs because of its operational simplicity as well as many other competitive advantages [47]. Although a variety of natural and synthetic materials, including activated carbon [48], biomaterials [49], fly ash [50], metal–organic frameworks [51], natural/modified clays [52, 53], nanomaterials [54], and zeolites [55] have been investigated as adsorbents for eliminating PCs, the development of affordable and recyclable adsorbents with sufficiently high adsorption capacities remains a critical challenge.

Over the past few years, biochar has emerged as a potential adsorbent material for the removal of PCs, especially due to its tunable surface chemistry, large specific

**Fig. 1** Fate and transport of PCs and their metabolites into transformed products following different sources and interdependent complex pathways. Reproduced with permission [19]. Copyright (2013), Elsevier Ltd. PCs Pharmaceutical compounds



surface area (SSA), and high porosity [56, 57]. Biochar can be classified depending on the type of waste residues utilized as feedstock. Although biochar shows excellent removal efficiency for PCs, its practical application is still limited by its surface chemistry and insufficient recyclability. As biochar production schemes typically utilize agro-industrial leftovers as feedstock, the adoption of green functionalization methods to overcome the aforesaid limitations is appealing both in terms of environmental and economic sustainability. In view of the aforementioned, the present review collates the latest progress in the application of biochar and its modified variants for the removal of PCs from wastewater. Specifically, it critically examines the existing technologies to eliminate PCs from wastewater, with a clear focus on biochar-mediated adsorption as a viable solution for the removal of PCs. Furthermore, the key merits of using biochar as adsorbents for the removal of PCs, different types of feedstocks exploited for biochar production, and optimization of biochar preparation have been discussed. It is anticipated that the review will particularly help to gain fundamental insights into biochar-mediated removal of PCs from aqueous systems via adsorption-based separation.

### Existing technologies for remediation of PCs with adsorption as an emerging one

There is an emergent need to mitigate the long-term consequences of PCs, which are introduced into wastewater through a wide range of channels. The development and

implementation of a global standard protocol for solving the issue of contamination of aquatic matrices with PCs are pressing needs of the hour. To this end, efficient removal technologies are already in place and can be employed to address PCs contamination to a considerable extent. In general, PCs from the aquatic environment can be treated using physical, chemical, and biological treatment methods [58]. The physical treatment methods include adsorption [59–61], flocculation–coagulation [62, 63], electrocoagulation [64], and RO [65]. On the other hand, chemical treatment options include precipitation, neutralization, and ion exchange. Biological treatment methods employ the use of microorganisms via an activated sludge process (ASP), trickling filters, and stabilization ponds. The biological treatment stage is the deciding factor for the uptake of these compounds. Generally, biological methods adopt bacterial, fungal, and algal culturing techniques to biodegrade the PCs. For instance, microalgae treatment processes simulate natural environment of the microorganisms, wherein enzymes secreted by the microorganisms are responsible for the removal of PCs through decomposition or phytoremediation. This method for PC removal is very effective only if fungal reactors are employed. Thus, these specialized reactors help in the removal of a wide array of pharmaceutical residues from wastewaters, such as anticancer drugs, beta-blockers, antibiotics, and anti-inflammatory drugs, with almost 100% efficiency [66]. The removal efficiency of PCs from wastewater depends upon the chemical structure of a molecule, which can be hydrophobic or hydrophilic in nature. Generally, the probability of a pharmaceutical molecule

being eliminated from an aqueous system increases with its hydrophobicity. Moreover, if the molecules are polar, their potential to be adsorbed on a solid surface diminishes and they are more likely to exhibit a higher water dissolving propensity. Therefore, the adsorption process requires more hydrophobic molecules and suspended particulate matter in the wastewater.

## ASP

In an ideal ASP, there are mainly two important parameters that play a vital role: sludge age and hydraulic retention time. Higher hydraulic retention time indicates the complexity of the pharmaceutical molecules in wastewater [67]. The key mechanism in ASP for pharmaceutical removal is sorption, where PCs accumulate on the surface of sludge solids according to their component speciation behavior. The concentration of PCs sorbed per liter of wastewater can be expressed by the following equation [68]:

$$C_{\text{sorbed}} = K_d \times SS \times C_{\text{dissolved}} \quad (1)$$

where  $K_d$  is the sorption coefficient or partition constant between the sludge and water phase, SS is the concentration of suspended matter, and  $C_{\text{dissolved}}$  is the concentration of material dissolved in the wastewater. The generic sequence for the extraction of PCs from wastewater through activated sludge treatment is as follows: stimulant drugs>metabolites>analgesics>antibiotics>anti-inflammatory>lipid regulators>NSAIDs>other PCs [66]. Trickling filters or bio towers integrated with ASP can be used. However, the pharmaceutical removal rate varies greatly depending upon the recalcitrant nature of the compound present in wastewater. More frequently, the artificial introduction of microorganisms on the sludge surface helps to remove PCs through mutual participation of dissolved oxygen in the solution, diverse species of microorganisms, and as biosolids formed in the process. As an example, Peng et al. [69] demonstrated removal rates of PCs in ASP by elucidating the biodegradation routes into three processes, viz., nitrification, COD degradation or, both nitrification and COD degradation. The study showed that heterotrophic degradation and adsorption were the dominant PC removal routes in ASP.

## Constructed wetlands

Constructed wetlands are simple eco-friendly treatment systems that are established based on the requirement of plants to thrive in aquatic environments and have significant contributions towards removing PCs from wastewater. There are some vital operational and design parameters of constructed wetlands that affect the decomposition of PCs. It includes the type of plant, their quantity, morphological features, bed

depth, bed dimensions, hydraulic loading rate, and organic loading rate. Unfortunately, constructed wetlands pose worrisome operational drawbacks concerning a larger footprint and higher retention time [70]. Notably, the efficiency for the elimination of four PCs, that is, DFC, IBP, carbamazepine (CBZ), and NPX in tropical constructed wetlands, has been investigated [71]. The study found that a narrow range of residence time is required for proper extraction of these compounds. In fact, CBZ and DFC appeared to be intractable compounds with minimum removal efficiency from the constructed wetland. However, recent work revealed that DFC and CBZ could achieve over 91% removal efficiency when natural zeolite was used as substrate [72]. In another notable contribution, Sanchez et al. [73] implemented an advanced oxidation process (AOP) as a post-treatment strategy with constructed wetlands to meet the simultaneous removal of studied PCs. However, such hybrid systems were able to treat selected PCs based upon the selective potential of catalyst performance. This shows that constructed wetlands sometimes can be a selective option for treatment of PCs, depending on their removal efficiencies as well as hydrophobic nature. Besides, sorption and photodegradation can be a possible complex pathway to degrade some PCs in wetlands.

## AOPs

Alternatively, there is also practice of tertiary treatment for the effective removal of PCs from wastewater via AOPs and produces oxygen-enriched reactive species, such as peroxide radicals, hydroxyl radicals, and superoxide radicals, in the aqueous phase [74]. This process proceeds with the help of catalyst and oxidizing agents, and upon mineralization of the contaminant generates  $\text{CO}_2$  and water. Specifically, numerous types of contaminants are oxidized by attacking reactive free radical sites. AOP takes place by coupling it with other treatments or itself using different oxidizing agents. Few individual or combination of any AOP can be ozone ( $\text{O}_3$ ), ozone/hydrogen peroxide in combination with ultraviolet (UV) radiation ( $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ ), ozone combined with  $\text{UV}/\text{H}_2\text{O}_2$ , photo-Fenton oxidation, and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ . Each of these AOPs contributes largely to the removal of PCs from wastewater and other matrices of the aquatic environment. Typically, PCs are oxidized to more harmful end products that persist in the aqueous phase [75]. In some cases, when the ozone dose is less than the requisite amount, the PCs may be transformed to complex byproducts, which are even more detrimental than the original compounds. This implies that an appropriate dosage must be decided to deal with different types of PCs. Additionally, high operation and maintenance costs are other disadvantages of the technology. The key distinguishing feature between ozonation and AOP is the functional role of catalyst. For ozonation, action on PCs occurs without the use of any catalyst whereas AOPs



involve the use of catalyst. When ozonation is employed to treat wastewater, AOP is more effective for some PCs and less effective for others. As an example, a rapid removal rate on the order of  $1 \times 10^5$  to  $1 \times 10^6$  was observed for PCs, such as CBZ, DFC, and SMX, during the ozonation process [76]. PCs, such as diazepam, and IBP, on the other hand, were comparatively found in the minimum range. Hence, it is recommended to couple ozonation with other treatment technologies because, attributed to its chemical nature, the reaction time of ozone varies with contaminant type, which in turn ultimately governs the treatment duration. More importantly, ozonation increases operational expenses and is an energy-intensive process [77]. Photolysis is another type of AOP for degrading PCs using natural or artificial light. This photodecomposition can be accomplished via two modes, i.e., direct photolysis or indirect photolysis [78]. The former occurs when there is a splitting of a molecule by the energy absorption mechanism (primarily upon exposure to UV light). In the latter case, excited states of highly reactive species, viz., hydroxyl radicals, singlet oxygen, hydrogen peroxide, etc., are produced. The primary reaction mechanism is photosensitization, where the species oriented towards light absorption are brought to their stable ground state from the triplet state. The key parameters that determine the efficiency of photocatalysis for PCs include the pH of the solution, feasibility of direct or indirect photolysis, level of concentration during the early stage of extraction, magnitude of radiation in terms of frequency and intensity and nature of the irradiated light.

### Membrane-based technologies

Membrane-based separation processes are extensively employed to eliminate PCs from a variety of aqueous matrices. In this technology, the removal mechanism of PCs varies based on the different therapeutic classes of PCs. Typically, pressure-driven membrane separation techniques are extensively employed to abate PCs via RO, ultrafiltration (UF), NF, and microfiltration. Among the different membrane treatment processes, UF offers numerous benefits, such as operational ease, lower energy consumption, and cost effectiveness. However, UF provides the lowest PCs removal efficiency [79]. Meanwhile, although NF and RO have the best removal efficiencies for PCs from water and wastewaters, the physicochemical properties of PCs, which are specifically governed by the solution chemistry of aquatic systems, are still a critical contributor in determining the overall effectiveness of NF [80]. In this context, Kim et al. [79] recently compared the retention rate and permeate flux of commercially available powdered activated carbon and UF activated biochar hybrid system towards selected PCs, such as IBP, 17  $\alpha$ -ethinyl estradiol (EE2), and CBZ. The study revealed that UF-activated biochar produced an

average retention rate of 41.40% and normalized flux of 0.85, indicating superior performance for target PCs. Therefore, the combination of membrane technologies with adsorption seems to be a judicious choice with respect to retention and fouling reduction. To deal with the high economics involved or to modify the other operational parameters, membrane separation technologies are mostly combined with other pharmaceutical removal methods, including photolysis, ozonation, adsorption, coagulation, and so on. Additionally, membrane bioreactors are the integration of two removal techniques, i.e., membrane separation technique and biological process. Secondary treatment tanks are replaced by membrane bioreactor to perform a similar function as ASPs. For instance, Rios-Miguel et al. [67] utilized membrane bioreactor inoculated with activated sludge for removal of six PCs, and the average removal efficiency decreased in the following order: acetaminophen (100%)>fluoxetine (50%)>metoprolol (25%)>diclofenac (20%)>metformin (15%)>carbamazepine (10%). Interestingly, the study found that the metformin removal percentage was over 80% when the process parameters (hydraulic retention time and initial concentration of PCs) were increased. Hence, the integrated design of the reactors optimized the removal efficiency of PCs. Poor performance due to fouling, pore blockage of membranes, and immediate replacement in case of rupture of membranes are some of the common problems associated with the practical application of membranes. Moreover, membrane technology is still an unattractive option due to the tremendous expense associated with the removal of PCs from aqueous environment.

### Electrocoagulation

Electrocoagulation involves the use of electricity to clean up wastewater contaminated with PCs [81]. The treatment approach involves chemical coagulation assisted by sacrificial electrodes undergoing oxidation–reduction reactions. Ideally, the material used to fabricate electrode should be non-poisonous, able to eliminate contaminants, and environmental friendly. Interestingly, the pattern for setting up the electrocoagulation-based reactor has a significant effect on the removal efficiency of a particular PCs. The key factors involved in the treatment process include pH, current density, retention time for electrolysis, electrolyte to be used, electrode alignment, and materials used to fabricate the electrodes [82, 83]. For instance, at a current density of  $20 \text{ mA cm}^{-2}$ , oxytetracycline hydrochloride was efficiently removed from the surface of both anodes (iron and aluminum) with removal efficiencies of 93.20% and 87.75%, respectively [84]. In another recent work, Bajpai et al. [85] investigated the removal of cefazolin using an electrocoagulation process, with a current density of  $16 \text{ mA cm}^{-2}$ , pH 8, iron as the electrode material, and an electrolysis time of

40 min. Moreover, the study estimated the removal efficiency of cefazolin as 86.74% via response surface methodology. Thus, it is evident that the electrocoagulation setup is easy to maintain, involves the use of inexpensive electrodes, can be operated regularly, and has the potential to deal with huge volumes of pharmaceutical wastewaters, as well as greater removal efficiency. However, electrocoagulation also has several limitations, such as high investment cost, continuous power supply, scale-up issues, electrode replacement, and technical feasibility with respect to its performance. Nevertheless, the combination of this technology with other treatment methods increases the rate of PCs removal. Although electrocoagulation works well for the removal of PCs, the prevailing drawbacks limit its widespread application.

## Adsorption

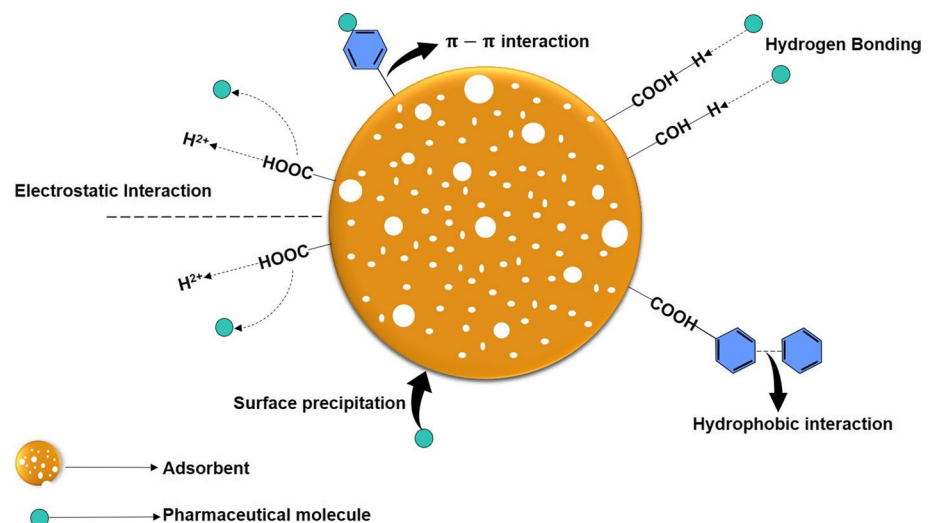
Among all the treatment techniques, adsorption can eliminate a wide array of PCs from wastewater. This technology is extremely amenable due to multiple advantages viz., operational ease [86], absence of toxic byproducts, scalability, and low cost [87]. This method, in addition, has the full capability to adsorb different PCs on the surface of the adsorbent. Any kind of adsorbent may act as a suitable site for the attraction of PCs. However, the adsorbent should be cost-effective with a high potential for the removal of contaminants from wastewater. The removal mechanism of pollutants is simple, whereby the adsorbate, such as PCs, migrates and adheres to a suitable reactive site on the periphery of the adsorbent and is thus removed from the aqueous medium. In general, the adsorbent holds the PCs through  $\pi$ - $\pi$  interactions, electrostatic interactions, hydrophobic interactions, surface precipitation, and van der Waals forces of attraction, as shown in Fig. 2. Eventually, during the natural sorption mechanism, when the

rates of adsorption and desorption are equal, a movable equilibrium condition is achieved. At this stage, the capacity of adsorbate to adsorb onto the preferred site becomes negligible, and it is assumed that the process of adsorption has reached its saturation, called the peak adsorption capacity. To attain a better understanding of the adsorption equilibrium conditions, adsorption isotherms are used to describe the adsorption data. The main objective of adsorption isotherms is to establish a clear link concerning the concentration of solute molecules adsorbed onto the solid phase with the corresponding equilibrium concentration in the liquid phase for a given temperature and pressure. Reaction kinetics help to investigate the rate of adsorption through the optimum selection of adsorbate and adsorbent. Thus, it is essential to choose the material for the adsorption of PCs in such a way that there is no detrimental effect on the environment. The involvement of favorable parameters, such as pH, concentration of the adsorbate, nutrients, and temperature of the media, governs the suitability of this process. Different adsorption isotherm and adsorption kinetic models have been developed by researchers to replicate the removal behavior of PCs employing biochar in aqueous environments, as listed in Table 2.

## Adsorption isotherms

Various isotherm models have been explored to determine the adsorption capacities of adsorbents. These include Langmuir, Freundlich, Sips, Redlich–Peterson (RP), Dubinin–Radushkevich, and Temkin. For instance, biochar synthesized from banana pseudostem fibers and date stone seeds was used to remove amoxicillin (AMX) and IBP, respectively. The adsorption equilibrium data showed good correlation with the Langmuir model [88,

**Fig. 2** Typical mechanism for adsorption of PCs



**Table 2** Summary of different theoretical models applied for predicting isotherm and kinetic data of biochar-mediated adsorption of PCs

Models	Equations	Model parameters	Biochar precursor	PC	References
<b>Adsorption isotherm models</b>					
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_L} + \frac{C_e}{q_L}$	$q_e$ (mg g <sup>-1</sup> ): Equilibrium adsorption capacity $q_L$ (mg g <sup>-1</sup> ): Maximum adsorption capacity $K_L$ (L mg <sup>-1</sup> ): Langmuir isotherm constant $C_e$ (mg L <sup>-1</sup> ): Equilibrium adsorbate concentration in solution	Date stone seeds Banana stem fibers Pomelo peel	Ibuprofen (IBP) Amoxicillin (AMX) Carbamazepine (CBZ)	[90, 91, 92]
Freundlich	$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e$	$K_F$ [(mg g <sup>-1</sup> ) (L mg <sup>-1</sup> ): Freundlich isotherm constant $n$ : Heterogeneity factor	Goose berry seed shells Municipal solid waste (MSW) <i>Gliricidia sepium</i>	Naproxen (NPX) Tetracycline (TC) Caffeine (CAF)	[93, 94, 95]
Sips	$q_e = \frac{q_s K_s C_e^{\frac{1}{m}}}{1 + K_s C_e^{\frac{1}{m}}}$	$q_s$ (mg g <sup>-1</sup> ): Maximum uptake of adsorbate per unit mass of adsorbent $K_s$ (L mg <sup>-1</sup> ) <sup>1/m</sup> ): Sips constant related to energy of adsorption $m$ : Sips parameter characterizing the system heterogeneity	Giant reed MSW	Amoxicillin (AMX) Ciprofloxacin (CFX)	[96, 97,
Redlich Peter-son (R–P)	$\ln(K_R \frac{C_e}{q_e} - 1) = \ln(\alpha_R) + \beta \ln(C_e)$	$K_R$ (L g <sup>-1</sup> ): Redlich–Peterson isotherm constant $\alpha_R$ and $\beta$ are constants used for fitting the model	Bovine bone Pine saw dust Pure glucose	Caffeine (CAF) Sulfamethoxazole (SMX) Paracetamol (PRC)	[98, 99, 29]
Dubinin–Radushk-evich (D–R)	$\ln q_e = \ln q_D - B \varepsilon^2$ $\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$	$q_D$ (mg g <sup>-1</sup> ): Theoretical isotherm saturation capacity $B$ (mol <sup>2</sup> kJ <sup>-2</sup> ): Dubinin–Radushkevich isotherm constant $\varepsilon$ (kJ mol <sup>-1</sup> ): Adsorption potential derived from Polanyi adsorption potential theory $R$ : Universal gas constant (8.314 J mol <sup>-1</sup> K <sup>-1</sup> ) $T$ (Kelvin): Temperature	Pomelo peel Pure glucose Cherry stalk Pomelo peel waste	Carbamazepine (CBZ) Paracetamol (PRC) Ciprofloxacin (CFX) Paracetamol (PRC)	[91, 29, 100, 29]
Temkin	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	$K_T$ (L g <sup>-1</sup> ): Equilibrium binding constant corresponding to the maximum binding energy $b$ : Temkin isotherm constant	Corn husk <i>Gliricidia sepium</i> Cherry stalk	Levofloxacin (LEV) and Tetracycline (TC) Caffeine (CAF) Ciprofloxacin (CFX)	[35, 95, 100]
<b>Adsorption kinetic models</b>					
Pseudo first order (PFO)	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$q_t$ (mg g <sup>-1</sup> ): Amount of adsorbate adsorbed at any time $t$ (min) $k_1$ (min <sup>-1</sup> ): PFO rate constant	Giant reed Pure Glucose	Amoxicillin (AMX) Paracetamol (PRC)	[96, 29]



**Table 2** (continued)

Models	Equations	Model parameters	Biochar precursor	PC	References
Pseudo second order (PSO)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> ): PSO rate constant	Giant reed Goose berry seed shells	Amoxicillin (AMX) Naproxen (NPX)	[96, 93]
Intra-particle diffusion (IPD)	$q_t = k_t t^{\frac{1}{2}}$	$k_t$ (mg g <sup>-1</sup> min <sup>-1/2</sup> ): IPD rate constant	Corn husk Textile effluent sludge Cherry stalk	Levofloxacin (LEV) and Tetracycline (TC) Ofloxacin (OFL) Ciprofloxacin (CFX)	[35, 101, 100]
Boyd's film diffusion	$2\pi - \pi^2 \frac{F(t)}{3}$ $- 2\pi(1 - \pi \frac{F(t)}{3})^{\frac{1}{2}}, 0 < F(t) > 0.85$ $B_t = -0.4977 - \ln(1 - F(t)), 0.86 < F(t) > 1$	$F(t)$ : Ratio of $q_t$ to $q_e$ corresponding to fractional achievement of equilibrium $B_t$ = Mathematical function of $F$	Bagasse biomass Cherry stalk	Tetracycline (TC) Ciprofloxacin (CFX)	[102, 100]
Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$	$\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> ): Rate of adsorption during the initial phase $\beta$ (g mg <sup>-1</sup> ): Desorption constant	Raw bamboo Pure glucose	Sulfamethoxazole (SMX) Pracetamol (PRC)	[103, 29]

89], suggesting that the adsorption is monolayer, adsorption of each molecule has equal activation energy, and that the adsorbate–adsorbate interaction is negligible [102]. On the other hand, Freundlich model showed an excellent fit to the adsorption isotherm data of tetracycline (TC) and NPX onto biochar synthesized from goose berry seed shells and municipal solid waste (MSW) [91, 92]. This result implied that numerous and diverse binding sites, each with a different free energy of sorption, were simultaneously involved in the adsorption process. Furthermore, the Sips isotherm can be used for modeling the adsorption in heterogeneous systems and overcoming the limitation of rising adsorbate concentrations associated with the Freundlich model [27]. For instance, the Sips isotherm was the best-fitting model for the adsorption of AMX and CFX onto biochar derived from giant reed and MSW, respectively [94, 95]. As such, at low adsorbate concentrations, the adsorption space accommodated more than one layer of adsorbates, whereas at high concentrations, the adsorbed molecules formed a single layer on the adsorbent surface.

### Adsorption kinetics

The kinetics of the adsorption process provide useful insights into the surface chemistry involved in the uptake of the adsorbate on the adsorbent. The kinetics establish a relationship between time and concentration and the phenomena

involved in the adsorption process. Table 2 shows the various kinetic models, viz., pseudo first order (PFO) model, pseudo second order (PSO) model, intra-particle diffusion model, Boyd's film diffusion model, and Elovich model, which have been exploited by researchers to describe the adsorption kinetics of PCs on biochar. Among these models, PSO is the best-fitting kinetic equation in most cases. For example, the PSO kinetic expression was found to be the best-fit expression to represent the kinetics of NPX and AMX onto activated biochar [91, 94]. This indicates that the rate-limiting step is chemisorption, and the adsorption rate is dependent on adsorption capacity of the adsorbent and not on the concentration of the adsorbate.

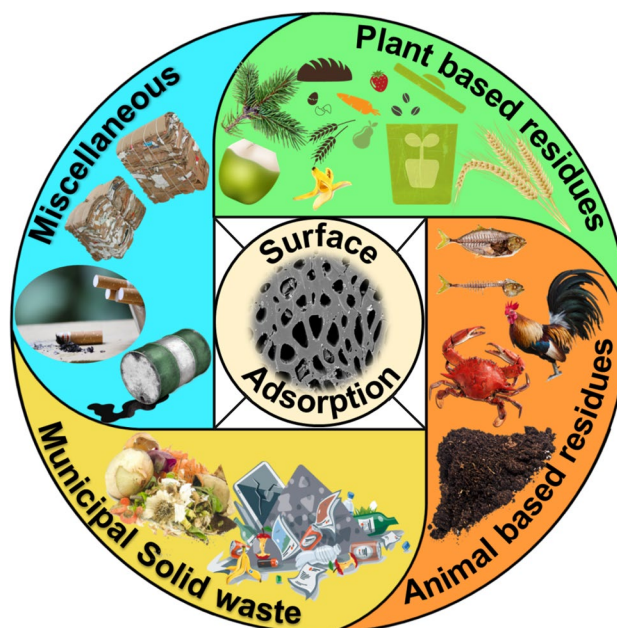
### Biochar as adsorbents for removal of PCs

A plethora of adsorbents, notably activated carbon [48], carbon nanotubes (CNTs) [104], graphene-based materials, biomaterials [49], fly ash [50], metal–organic frameworks [51], zeolites [55], clay minerals [52, 53], and biochar [105], have been studied for the removal of PCs. Activated carbon is the most common and widely studied adsorbent for the removal of PCs like KETO, IBP, NPX, and DFC [106]. However, when the regeneration issue is taken into account, their application becomes expensive and constrained. Similarly, CNTs offer excellent SSA and tunable porosity to

remove organic contaminants as well as PCs from wastewater. Some adsorption studies employed single-walled CNTs, while other utilized multi-walled CNTs [107, 108] for adsorption of IBP, triclosan (TCS), and TC from aqueous solutions. Another well-known allotrope of carbon, i.e., graphene and its derivatives, has been found to be promising adsorbents for removal of PCs [109]. Typically, the adsorption process is highly accelerated using graphene oxide as an adsorbent material, which can be attributed to its surface oxygen functionalites. The adsorption of ACE, CAF, and aspirin from wastewater using graphene plates as an adsorbent material has shown excellent removal efficiencies [110]. In another recent work by Mahmoodi et al. [109], clayey adsorbent materials gained importance due to their natural availability, cost effectiveness, extreme mechanical as well as chemical stability, large pore sizes, higher SSA, and good ion exchange capacity. When clays are used for adsorption of PCs, surface charge phenomena are dominant. For example, montmorillonite (MMT), bentonite, kaolinite, fullers earth, and illite are the most recognized category of clays and are used for the adsorption of pollutants. The concentration of different pharmaceutical products present in the tested wastewater sample was assessed using clay minerals as adsorbents. It was found that the concentration of DFC and tramadol was dominant than other PCs due to the greater probability of favorable physiochemical properties of clayey material towards these PCs [52]. However, the urgent need for a sustainable adsorbent material with the least environmental impact has been a potential solution to address the limitations of commercially available adsorbents. Hence, biochar-based materials as adsorbents appear to be a green solution for mitigating the PCs removal through adsorption-based technology.

In particular, among the different available adsorbents, biochar can be considered as an ideal substitute to remediate PCs from wastewater [56, 57]. Biochar as an adsorbent provides the maximum benefits to wastewater treatment because of its physiochemical properties. The cost effectiveness, improved sorptive capacity, and flexibility of biochar to contaminants obviate the need for intensive application of activated carbon as well as provide inexhaustible opportunities for the removal of PCs from wastewater. The International Biochar Initiative states biochar as “a material attained from the thermo-chemical carbonization of biomass in an oxygen-limited environment.” Biochar is a green material among other adsorbents since the origin is through the thermal route, such as pyrolysis, torrefaction, gasification, and carbonization, using organic waste from different sources (agriculture waste, green cover waste, municipal waste) [111, 112]. The entire aforementioned thermal technologies need an oxygen-limited atmosphere to generate biochar, and biochar production from these individual thermal routes allows flexibility of operation in terms of different

parameters [113]. When biochar is produced via the pyrolysis route, it is predominantly carbonaceous and demonstrates good porosity [114]. During primary reaction phase, initially the narrow range volatile components are liberated, then intermediate compounds which are aromatic by origin are obtained [103], and finally solid fraction is received as biochar. Indirectly, biochar can also be derived using hydrothermal carbonization, but it is usually not preferred as it is time consuming. Hydrothermal carbonization is an aqueous substrate process where biochar is generated and is composed of aliphatic rings [103]. Moreover, immense energy via two step conversion needs to be applied while obtaining biochar through this route, as hydrochar is the initial solid output. Another carbonization technique uses microwave radiation to produce biochar with better porosity, greater SSA, and optimized reactive conditions [115]. Biochar has two activation modes in place (physical and chemical), which helps researchers to improve the adsorption propensity towards a contaminant of interest. Before activation, biochar is synthesized from different feedstocks, viz., plant residue-derived biochar, animal waste-derived biochar, municipal waste-derived biochar, and other miscellaneous sources, as shown in Fig. 3. Generally, the molecular size of PCs requires mesoporous biochar as an adsorbent for the effective elimination of trace components from wastewater. However, very narrow mesopores or PCs with a humongous size may restrict the adsorption path length. Thus, surface modification of biochar is strongly suggested, to ease the treatment of recalcitrant compounds, such as personal care



**Fig. 3** Types of feedstocks for biochar production for adsorption of PCs

products and PCs. In recent years, biochar has been modified and transformed into composites to increase the adsorption capacity of contaminants. The net performance is assessed based on changes observed in its carbonaceous structure. Higher variation in the carbon morphology of biochar indicates less recovery of target PCs from wastewater. The criteria for the selection of biochar must include the economic viability and environmental sustainability of the biomass feedstock. Overall, biochar serves as a sustainable adsorbent material to handle the wide variety of emerging contaminants found in different environmental matrices.

### Biochar from various feedstocks for removal of PCs

Biochar has been successfully employed to remove PCs from aqueous matrix. Biochar, a low cost and effective adsorbent, has gained tremendous attention and application in eliminating PCs from various water matrices. Table 3 lists various PCs and their adsorptive removal by different biochars and the corresponding adsorption mechanism.

#### Plant residue-derived biochar

Various plant derived biomasses have been used as feedstocks for synthesizing biochar for the adsorption of PCs. Plant residues are readily available, inexpensive, and renewable in nature. The properties of biochar depend upon the feedstock characteristics and composition. For example, most plant residues constitute lignin (27%), cellulose (43%), and hemicellulose (20%), which affect the elemental composition of biochar. Biochar produced from lignocellulosic biomass has a higher carbon content. Various plant residues like corncobs [116], pine needles [117], rice hulls [118], coconut shells [22], banana pseudostem [89], wood chips [23], oil palm fiber [28], pomelo peels [29], moringa seed powder [27], walnut shells [26], date stone seeds [88], mung bean husks [119], wood apple (*Aegle marmelos*) fruit shells [24], eucalyptus globulus wood [32], and hickory chips [33], have been used as feedstocks for the production of biochar for the adsorption of various PCs.

#### Animal waste residue-derived biochar

Animal wastes like swine manure, chicken feathers, bovine bones, fish scales, etc., have been used as feedstocks for biochar production. These animal waste-derived biochars have proven effective in the adsorption of PCs [33]. For instance, biochars from bovine bones were used for adsorption of CAF. The bone biomass was pyrolysed at 650 °C and co-precipitated into a composite using clay minerals [96].

### MSW -derived biochar

Solid waste generation is increasing exponentially mainly because of the increased population and improper waste management and treatment strategies. Among many treatment methods, thermally converting waste into biochar via pyrolysis has attracted widespread interest from the research community. This solid waste-derived biochar has been applied for environmental remediation. Indeed, studies have shown the adsorption of various PCs on biochar derived from MSW [30, 120, 121], food and garden waste [124], flower waste [92], sludge from textile effluent treatment plants [99], etc.

### Engineered and modified biochar

Numerous modifications have been made to the structure of biochar to improve its adsorption capacity. These modification schemes have shown significant changes in the properties of biochar, and therefore influence the adsorption mechanism. Different biochar modification methods for enhanced adsorption of PCs include physical modifications [125, 126], acid–base modification [127], ball milling [128], clay–biochar composites [121], and metal–biochar composites [129].

#### Physical activation

Pyrolysis involves the restriction and limitation of oxygen to develop internal pores in biochar. Biochar can be physically activated by subjecting it to oxidizing agents, usually steam or carbon dioxide, at varying temperatures. Physical activation results in the enhancement of the physico-chemical properties and adsorption capacity. In particular, it enhances the SSA, total pore volume, and average pore size, as well as enriches the surface chemistry of biochar [127]. For example, biochar synthesized from apple shell feedstock was steam activated [24]. The pristine biochar had an SSA of 4.4 m<sup>2</sup> g<sup>-1</sup>. In contrast, steam activation resulted in an SSA of 308 m<sup>2</sup> g<sup>-1</sup>. The steam activation also resulted in creation of micropores and altered the chemical skeleton of the biochar. These changes were also evident from the pore volume calculations, as the steam-activated biochar had a pore volume of 0.384 cm<sup>3</sup> g<sup>-1</sup>, whereas the pristine biochar had a pore volume of only 0.184 cm<sup>3</sup> g<sup>-1</sup> [24].

#### Acid–base modification

Acid or alkaline modifications are carried out to change the surface characteristics of biochar. Chemical activation increases the SSA and pore volume, and pores are also concentrated in a smaller pore size range. As a notable example, chemical activation of swine manure biochar increased the SSA from 227.56 m<sup>2</sup> g<sup>-1</sup> to 319 m<sup>2</sup> g<sup>-1</sup>. It also resulted in

**Table 3** Summary of the adsorption potential of biochar and modified biochar towards different types of PCs

PCs	Feedstock	Pyrolysis conditions	Modification scheme	Specific surface area ( $S$ , $m^2 g^{-1}$ ) and total pore volume ( $V$ , $cm^3 g^{-1}$ )	Isotherm model	Kinetic model	Adsorption conditions	Adsorption capacity ( $mg g^{-1}$ )	References
Amoxicillin (AMX)	Banana pseudostem	350 °C for 2 h at 10 °C $min^{-1}$	CoFe <sub>2</sub> O <sub>4</sub> impregnation	$S=100.9$	L	PSO	AD=50 mg L <sup>-1</sup> , pH=7, $T=25$ °C	99.99	[89]
		650 °C for 2 h at 10 °C $min^{-1}$		$S=190.5$	L	PSO	AD=50 mg L <sup>-1</sup> , pH>7, $T=25$ °C	99.76	[28]
Acetaminophen (ACE)	Oil palm fiber	550 °C for 30 min at 5 °C $min^{-1}$	ZnCl <sub>2</sub> impregnation	$S=76.050$ $V=0.12$	F	PSO	AD=1 g L <sup>-1</sup> , pH=3	7.3	[23]
		800 °C for 7 h		$S=841$	L	PSO	AD=0.2 g, $C_0=100$ mg L <sup>-1</sup> , pH=6, $T=25$ °C	196	[29]
	Pomelo peels	700 °C for 3 h	–	$S=1033$	L	E	AD=0.5 g L <sup>-1</sup> , pH=7, $t=2$ h	147	[29]
	Pure glucose	900 °C for 3 h	Pre-pyrolysis and hydrothermal treatment	$S=1292$	L	E	AD=0.5 g L <sup>-1</sup> , pH=7, $t=2$ h	286	[28]
Cephalexin (CPX)	Oil palm fiber	550 °C for 30 min at 5 °C $min^{-1}$	ZnCl <sub>2</sub> impregnation	$S=76.050$ $V=0.12$	L	PSO	AD=1 g L <sup>-1</sup> , pH=3	7.9	[31]
Ciprofloxacin (CFX)	Used tea leaves	450 °C at 30 min	–	$S=8.06$ $V=0.01$	L	PSO	pH=6 and $T=40$ °C	238.1	[116]
		600 °C for 2 h	–	$S=306$	L	PSO	pH=4	0.4	[30]
	MSW	450 °C for 4 h at 15 °C $min^{-1}$	–	$S=4.33$	H	PSO	AD=1 g L <sup>-1</sup> , pH=7, $C_0=25$ g L <sup>-1</sup>	122.16	[117]
			Composite with MMT	$S=6.51$	H	E	AD=1 g L <sup>-1</sup> , pH=7, $C_0=25$ g L <sup>-1</sup>	167.36	[96]
Caffeine (CAF)	Pine needles	650 °C	Oxidized with boiling nitric acid	NA	L	PSO	AD=0.05 g, $T=40$ °C, pH=4	6.54	[118]
	Bovine bone	650 °C	AlCl <sub>3</sub> and MgCl <sub>2</sub> loading	$S=46.3$ $V=0.12$	RP	PSO	$t=20$ min, $T=40$ °C	26.21	[27]
Sodium diclofenac (SD)	Rice hull	Torrefied at 350 °C for 1 h	–	NA	L	PSO	AD=0.5 g, pH=2, $C_0=100$ mg L <sup>-1</sup>	3.3	[99]
	Moringa seeds powder	450 °C for 2 h at 10 °C $min^{-1}$	Chemical activation with H <sub>3</sub> PO <sub>4</sub>	NA	SM	PSO	AD=0.4 g L <sup>-1</sup> , pH=5	100.87	[99]
Ofloxacin (OFL)	Sludge of textile effluent treatment plant rich in iron chloride	400 °C for 4 h at 10 °C $min^{-1}$	–	$S=91.00$	RP-F	IPD	AD=5 g L <sup>-1</sup> , $T=25$ °C, pH=6, $t=5$ h	19.7	[99]

Table 3 (continued)

PCs	Feedstock	Pyrolysis conditions	Modification scheme	Specific surface area ( $S$ , $m^2 g^{-1}$ ) and total pore volume ( $V$ , $cm^3 g^{-1}$ )	Isotherm model	Kinetic model	Adsorption conditions	Adsorption capacity ( $mg g^{-1}$ )	References
Ketoprofen (KETO)	Walnut shell	600 °C for 2 h	Microwave treatment of walnut shell and $FeCl_3$	$S=786$	L	PSO	$AD=0.5 g L^{-1}$ , $T=25 °C$ , $pH=3$ , $t=2 h$	444	[26]
Levofloxacin (LEV)	Corn husks	300 °C for 1 h at 5 °C $min^{-1}$	Pre-pyrolysis $FeCl_3$ impregnation	$S=112.45$	L	IPD	$AD=8 g L^{-1}$ , $C_0=200 mg L^{-1}$	56.6	[35]
			Post-pyrolysis $FeCl_3$ impregnation	$S=94.9$	L	PSO	$AD=8 g L^{-1}$ , $C_0=200 mg L^{-1}$	273.7	
Ibuprofen (IBP)	Coconut shell	450 °C for 1 h	Steam activation at 550 °C	$S=726$	L	PFO	$AD=2.66 g L^{-1}$ , $pH=2$ , $C_0=20 mg L^{-1}$ , $T=20 °C$ , $t=18 h$	9.69	[22]
			Chemical activation with $H_3PO_4$	$S=805$				12.16	
	Date stone seeds	700 °C for 1 h	Steam activation	$S=513$ , $V=0.2$	L	PSO	$AD=3 g L^{-1}$ , $pH=2$ , $C_0=20 mg L^{-1}$ , $T=20 °C$	9.69	[88]
			Chemical activation with $H_3PO_4$	$S=342$ , $V=0.13$	L	PSO		12.16	
	Wood apple fruit shell	650 °C for 1 h at 65 °C per 15 min	–	$S=4.4$	L	PSO	$AD=0.33 g L^{-1}$ , $pH=3$ , $T=15 °C$	5	[24]
			Steam activation	$S=308$	L	PSO	$AD=1 g L^{-1}$ , $pH=2$ , $T=20 °C$	12.65	
	Wood chips	800 °C for 7 h	–	$S=841$	L	PSO	$AD=0.2 g$ , $C_0=100 mg L^{-1}$ , $pH=6$ , $T=25 °C$	132	[23]
	Mung bean husk	550 °C for 1 h at 55 °C per 15 min	Steam activation at 650 °C	NA	L	PSO	$AD=0.1 g L^{-1}$ , $pH=2$ , $C_0=20 mg L^{-1}$ , $t=2 h$ , $T=20 °C$	59.76	[119]
Naproxen (NPX)	Walnut shell	600 °C for 2 h	Microwave treatment of walnut shell and $FeCl_3$	$S=786$	L	PSO	$AD=0.5 g L^{-1}$ , $T=25 °C$ , $pH=3$ , $t=2 h$	533	[26]



Table 3 (continued)

PCs	Feedstock	Pyrolysis conditions	Modification scheme	Specific surface area ( $S$ , $m^2 g^{-1}$ ) and total pore volume ( $V$ , $cm^3 g^{-1}$ )	Isotherm model	Kinetic model	Adsorption conditions	Adsorption capacity ( $mg g^{-1}$ )	References
Tetracycline (TC)	Rice straw	700 °C for 2 h	Chemical activation with $H_3PO_4$	$S=372.2$ $V=0.23$	L	PSO	$T=25$ °C, $pH=9$	552	[120]
	Swine manure	700 °C for 2 h	Chemical activation with $H_3PO_4$	$S=319.04$ $V=0.25$	L	PSO	$T=25$ °C, $pH=9$	365.4	
	MSW	500 °C for 30 min	Pre-pyrolysis treatment with MMT	$S=8.72$	F	PSO	$AD=2$ $g L^{-1}$ , $pH=7$ , $t=12$ h $C_0=20$ $mg L^{-1}$	77.96	[121]
	Food and garden waste	300 °C for 12 h	–	NA	F	E	$AD=5$ $g L^{-1}$ , $C_0=100$ $mg L^{-1}$ , $pH=7$	9.45	[92]
	Rice straw	700 °C for 2 h at 26 °C $min^{-1}$	–	$S=27.66$ $V=0.06$	L	NA	$AD=60$ mg, $T=25$ °C, $pH=5.5$	14.16	[122]
Salicylic acid (SA)	Walnut shell	600 °C for 2 h	Microwave treatment of walnut shell and $FeCl_3$	$S=786$	L	PSO	$AD=0.5$ $g L^{-1}$ , $T=25$ °C, $pH=3$ , $t=2$ h	683	[26]
Sulfamethoxazole (SMX)	Eucalyptus globulus wood	400 °C for 2 h at 11 °C $min^{-1}$	Chemical activation with $H_3PO_4$	NA	L	NA	$T=(25\pm0.5)$ °C	28.29	[32]
	Raw bamboo	450 °C for 2 h	Ball milling	$S=299$	L	E	$AD=0.3$ $g L^{-1}$ , $T=25$ °C, $pH=3$ , $t=2$ h	25.7	[33]
Sulfamethazine (SMT)	Tea waste	700 °C for 2 h at 7 °C $min^{-1}$	Steam activation	$S=421.31$	L	NA	$pH=3$	33.81	[123]
	Eucalyptus globulus wood	400 °C for 2 h at 11 °C $min^{-1}$	Chemical activation with $H_3PO_4$	NA	L	NA	$T=(25\pm0.5)$ °C	20.71	[32]
Sulfapyridine (SPY)	Hickory chips	450 °C for 2 h	–	$S=299$	L	E	$AD=0.3$ $g L^{-1}$ , $T=25$ °C, $pH=3$ , $t=2$ h	58.6	[33]

A adsorption capacity, AD adsorbent dose,  $C_0$  initial adsorbate concentration, E Elovich model, F Freundlich isotherm model, H Hill isotherm,  $h$  hour, IPD intra-particle diffusion model, L Langmuir, MMT montmorillonite, NA not available, PFO pseudo first order, PSO pseudo second order, RP Redlich–Peterson isotherm, S specific surface area determined from  $N_2$  adsorption/desorption measurements according to the Brunauer–Emmett–Teller equation, T temperature, t time, V total pore volume

a 79% increase in pore volume post-activation [120]. The most commonly used acids in acid activation are phosphoric ( $\text{H}_3\text{PO}_4$ ), sulfuric ( $\text{H}_2\text{SO}_4$ ), nitric ( $\text{HNO}_3$ ), and hydrochloric (HCl) acids. For alkali activation, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), potassium permanganate ( $\text{KMnO}_4$ ), and ammonium persulfate [ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ] are commonly used. Furthermore, the leading cause of the changes in the acid–alkali-treated biochar is the creation of additional surface active sites on the biochar surface, mainly due to the removal of minerals and other silicates [117].

### Ball milling

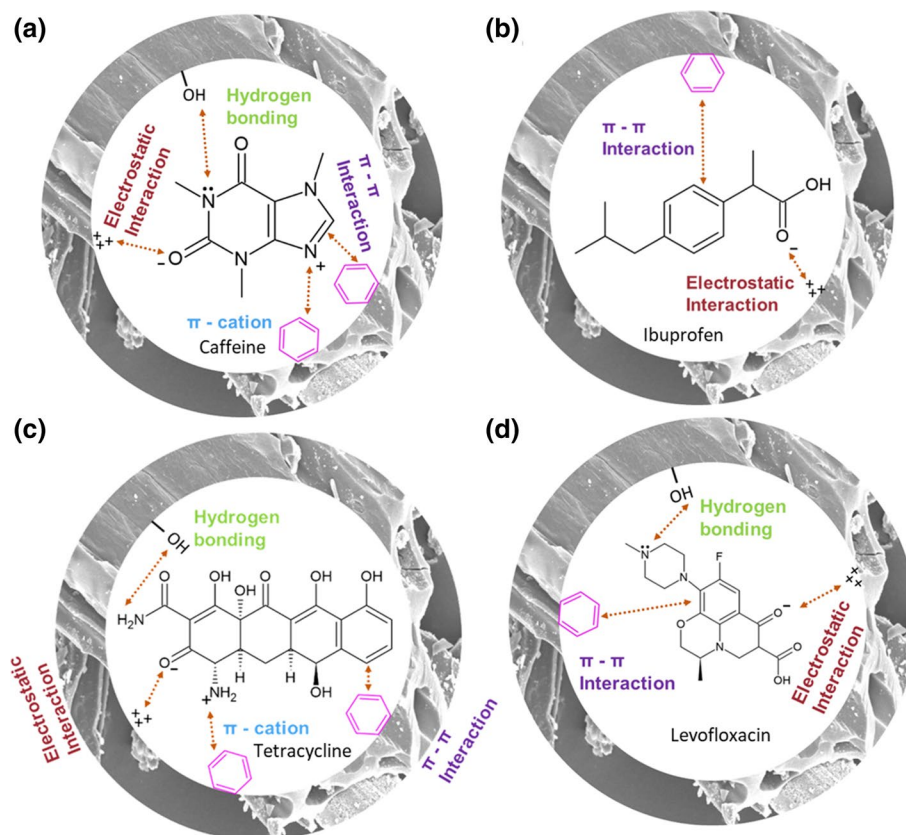
The grinding of biochar in a solid state process to nanometric size in a ball mill is considered a green modification method for biochar engineering. Ball milling enhances biochar's adsorption efficiency [57] due to an increase in SSA, opening of pore structures, and alteration of surface functional groups, all of which promote  $\pi$ – $\pi$  and electrostatic interactions [130]. For example, biochar derived from wood chips was ball milled, which resulted in an SSA of  $841 \text{ m}^2 \text{ g}^{-1}$ . Also, the optimal ball milling conditions for the maximum adsorption of PCs, such as ACE, IBP, and SA, were determined by changing the biochar-to-ball weight ratio to 1:5 and a milling time of 5 h, resulting in higher

efficacy. Ball milling also results in a change in the pore network. The macropores in biochar are reduced, and the proportion of mesopores usually increases to many folds, which makes the diffusion of adsorbates more favorable [23, 57]. Therefore, ball milling changes physicochemical properties, including greater external and internal surface areas and more acidic surface functional groups than pristine biochar [131].

### Clay–biochar composites

Impregnating biochar with specific materials, such as clay, minerals, and metals, results in the attainment of specific characteristics due to their synergistic effect. Generally, MMT, kaolinite, and palygorskite are impregnated onto biochar. The biochar-clay composites have been successfully employed for the adsorption of various PCs. For instance, in the adsorption behavior of MSW-derived biochar–MMT composite, the enhanced adsorption was due to enhanced active sites offered from the biochar and the clay mineral. Up to 40% increase in CFX adsorption onto the composite was observed compared with pristine biochar [30]. The study revealed that MSW-derived biochar composite could adsorb aromatic CFX molecules. Figure 4 shows the interaction mechanism between the CFX molecules and

**Fig. 4** Adsorption mechanism of (a) caffeine (CAF), (b) ibuprofen (IBP), (c) tetracycline (TC), and (d) levofloxacin onto biochar



the biochar-based composite. The electrostatic attraction between CFX and MMT leads to  $\pi$ - $\pi$  electron donor-acceptor interactions with the MSW-biochar [95].

### Metal-biochar composites

Various metals and their oxides (MgO, MnO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO) and hydroxides (Al(OH)<sub>3</sub>, Mg(OH)<sub>2</sub>) are commonly used in the synthesis of metal-biochar composites. This impregnation changes the negative surface charge (characteristic of biochar) to positive (characteristic of metal oxides). For example, Fe<sub>2</sub>O<sub>3</sub> impregnation of biochar resulted in an SSA of 786 m<sup>2</sup> g<sup>-1</sup>. The energy dispersive X-ray spectroscopy analysis showed the following composition: 68.75% carbon, 23.37% oxygen, and 7.23% iron. The addition of iron on the surface of biochar also resulted in the appearance of several new functional groups. Furthermore, the textural and morphological properties differed from those of pristine biochar, significantly impacting its applicability as an adsorbent [26].

### Biochar as a potential adsorbent for removal of PCs

Various pristine and modified biochars have been used for the adsorption of several PCs, which are described as follows:

#### Amoxicillin

AMX, C<sub>16</sub>H<sub>19</sub>N<sub>3</sub>O<sub>5</sub>S, is a  $\beta$ -lactam antibiotic used for treating various bacterial infections and has been detected in surface waters, as well as domestic and industrial wastewaters with varying concentrations. Studies have reported the presence of AMX in domestic and hospital effluents, as up to 80% of AMX is excreted through urine from the human body. Thus, it is vital to remove AMX residues. AMX is amphoteric in nature due to -NH<sub>2</sub>, -COOH, and -OH functional groups. Various adsorbents have been investigated for the removal of AMX from aqueous media, such as palm bark, almond shell ashes, chitosan beads, bentonite, graphene oxide, natural phosphate rock, grape and wine slurry waste, activated carbon from olive stones, pomegranate wood, guava seeds, and olive kernel [132]. Among these, biochar has been the most widely studied adsorbent because of its many interesting properties. In a notable study [89], banana pseudostem fibers collected from the Rabat region of Morocco were used for the preparation of biochar at a temperature of 350 °C and 650 °C for 2 h. The as-synthesized biochar was further impregnated in situ with CoFe<sub>2</sub>O<sub>4</sub> nanocomposites by co-precipitation process. This resulted in development of functional characteristics

like mesoporous structure, high SSA, and excellent magnetic characteristic. This was further verified using 50 mg of the as-synthesized composite, resulting in an adsorption capacity of 99.99 mg g<sup>-1</sup> at neutral pH. The PSO and Langmuir models were best fit for adsorption kinetics and isotherms, respectively, indicating monolayer adsorption of AMX onto the surface of magnetic biochar that was governed by electrostatic interactions,  $\pi$ - $\pi$  stacking, and hydrogen bonding.

#### Acetaminophen

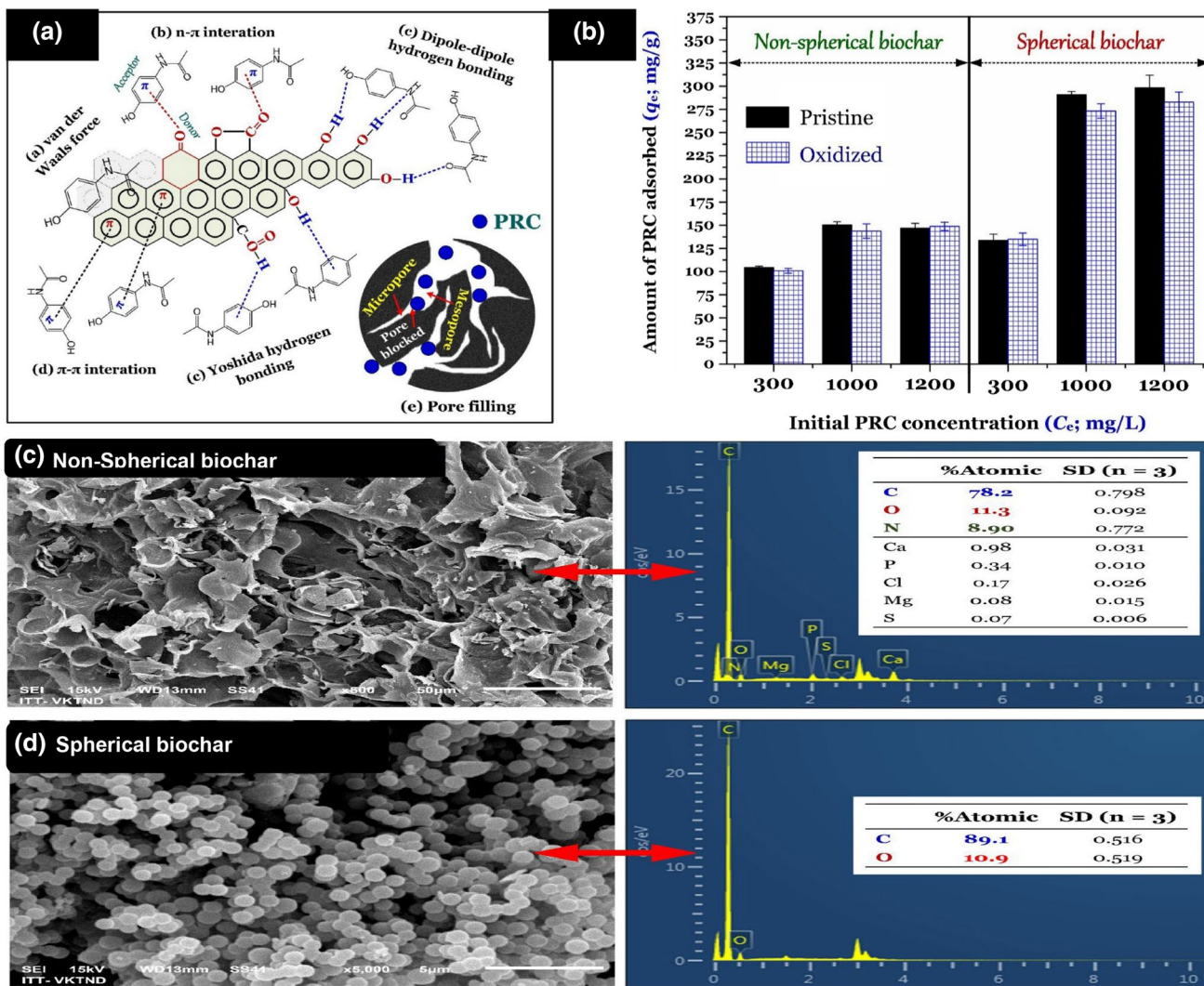
ACE, C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>, also known as paracetamol, is a common analgesic and anti-inflammatory drug used for both humans and animals. ACE is readily available, does not require a medical prescription, and is thus consumed worldwide. According to the "Global Acetaminophen Market Insights, forecast to 2025" report [29], there will be a tremendous increase in the production of paracetamol, with China and India contributing almost 64.40% and 21.20%, respectively, with an estimated 780 million dollars market by 2025. The human excreta contains up to 90% unmetabolized ingested ACE. In addition, the concentration of ACE in various environmental regimes like surface waters ((0.055±0.051)  $\mu$ g L<sup>-1</sup>), effluents from European sewage treatment plants (6  $\mu$ g L<sup>-1</sup>), USA natural waters (10  $\mu$ g L<sup>-1</sup>), Tyne River in the UK (65  $\mu$ g L<sup>-1</sup>) and raw hospital effluents (150  $\mu$ g L<sup>-1</sup>), is a matter of concern and poses risks to environmental quality, as well as animal and human health, and thus requires proper remediation mechanisms [133]. Biochar obtained from various feedstocks like oil palm fiber, wood chips, pomelo peels, pure glucose, MSW, etc., has been used for adsorption of ACE in the aqueous media [28]. For example, oil palm fiber biochar impregnated with ZnCl<sub>2</sub> post-pyrolysis showed a maximum adsorption uptake of 7.3 mg g<sup>-1</sup>. The ACE-adsorbent interaction was best described by the Freundlich isotherm at an acidic pH of 3. Oxygenated functional groups like carbonyl/ketone, carboxyl, and phenol on the oil palm fiber-derived biochar provided favorable conditions for hydrogen bonds and stronger  $\pi$ - $\pi$  interactions with ACE [28]. In another study, commercially available biochar derived from wood chips via pyrolysis at 800 °C for 5 h and 7 h, had SSAs of 477 m<sup>2</sup> g<sup>-1</sup>, and 841 m<sup>2</sup> g<sup>-1</sup> respectively, and was employed for ACE adsorption. In this study, the biochar was subjected to wet ball milling with 30 g milling balls, resulting in the destruction and alteration of the micropore network. This ball milling process affected the adsorption of ACE, indicating less favorability for the diffusion of ACE in micropores compared to mesopores. Moreover, temperature and pH are significant operating parameters affecting the adsorption process of ACE onto biochar [23]. Furthermore, studies have been carried out investigating the

shape of biochar and its effect on ACE adsorption behavior. For example, a study used non-spherical and spherical biochar (Fig. 5a, b) for ACE removal from aqueous environment. The biochar with a non-spherical texture was derived from pomelo peels, and the spherical biochar was derived from pure glucose. Both spherical and non-spherical biochars exhibited sizeable SSAs of 1033 m<sup>2</sup> g<sup>-1</sup> and 1292 m<sup>2</sup> g<sup>-1</sup>, respectively. Batch adsorption experiments demonstrated 286 mg g<sup>-1</sup> as the maximum adsorption capacity for spherical biochar and 147 mg g<sup>-1</sup> for non-spherical biochar. The study also concluded that the ACE removal mechanism mainly involved pore filling,  $\pi$ - $\pi$  interactions, hydrogen bonding, and van der Waals forces, as depicted in Fig. 5c. Furthermore, upon oxidation of biochar, a slight decrease was seen in the

amount of ACE adsorbed in comparison to the unoxidised counterparts (Fig. 5d), revealing the principal role of  $\pi$ - $\pi$  interactions in the adsorption process [29].

### Cephalexin

CPX, C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>S, is a  $\beta$ -lactam antibiotic within the class of first-generation cephalosporins, and can treat several bacterial infections. In a notable study, biochar synthesized from oil palm fiber was impregnated with ZnCl<sub>2</sub> post-pyrolysis, and was employed to remove CPX. This ZnCl<sub>2</sub>-biochar composite showed a maximum adsorption uptake of 7.9 mg g<sup>-1</sup>. The adsorption process was affected by variations in pH. It was optimum at an acidic pH of 3 due to stronger hydrogen bonding, an effective interface



**Fig. 5** (a) Adsorption mechanism of PRC (ACE) onto spherical biochar and non-spherical biochar; (b) comparison of adsorption capacities of PRC (ACE) onto the pristine and oxidized biochar samples at different initial

PRC concentrations; SEM-EDS of (c) non-spherical biochar derived from the pomelo peels; and (d) spherical biochar derived from the pure glucose. Reproduced from [29] with permission, Copyright 2020, Elsevier Ltd



with lone pair oxygen atoms, and higher  $\pi$ - $\pi$  interactions [28].

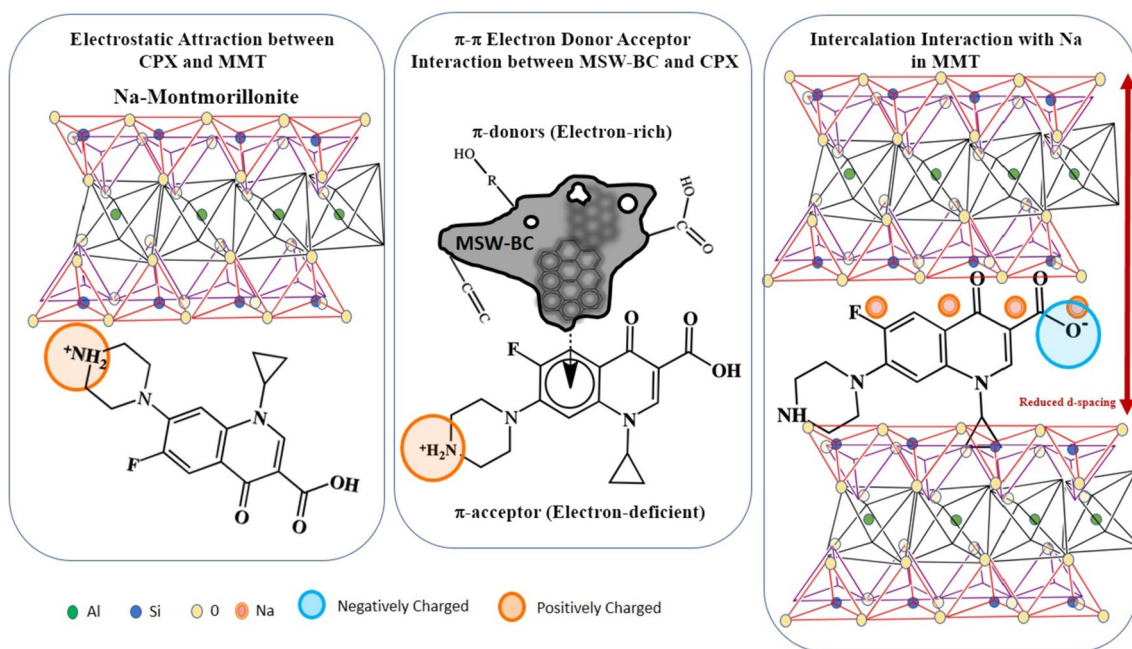
### Ciprofloxacin

CFX,  $C_{17}H_{18}FN_3O_3$ , is a third-generation fluoroquinolone antibiotic that is most commonly used as an antimicrobial agents in developing countries. CFX has low biodegradability; thus, its residues significantly impact the ecosystem and have been detected in water and wastewater. For example, in hospital effluents from Vietnam, Brazil and India, CFX has been found in the range of  $0.6$ – $53.3 \mu\text{g L}^{-1}$ ,  $32$ – $99 \mu\text{g L}^{-1}$  and  $2.2$ – $236.6 \mu\text{g L}^{-1}$ , respectively [116]. High concentrations of CFX in effluents from drug production plants with up to  $31 \text{ mg L}^{-1}$  have also been reported [31]. Researchers worldwide have recently investigated the adsorption of CFX on various biochars. Biochar from agricultural residues like corncobs, spent tea leaves, MSW, etc., are gaining attention for CFX removal. Corncob, an agricultural residue, pyrolysed at  $600 \text{ }^\circ\text{C}$  for 2 h, had an adsorption capacity of  $399.6 \mu\text{g g}^{-1}$  on the basis of the Langmuir isotherm model. The corncob-based biochar had an SSA of  $306 \text{ m}^2 \text{ g}^{-1}$  and followed PSO kinetics for CFX adsorption [116]. Similarly, biochar derived from used tea leaves at  $450 \text{ }^\circ\text{C}$  had excellent CFX absorption ability at  $40 \text{ }^\circ\text{C}$  and pH of 6. The adsorption capacity was  $238.10 \text{ mg g}^{-1}$ , which mandated the significance of temperature and pH as operating parameters. The adsorption mechanism mainly involved  $\pi$ - $\pi$  interactions, hydrogen bonding, and electrostatic attraction [31].

Modified biochar has shown better adsorption capacities than pristine biochar for the adsorption of CFX. For example, biochar–MMT composite provided more active sites for better adsorption of CFX. The increased active sites were a synergistic result of biochar and clay interactions, exhibiting greater CFX sorption compared to pristine biochar. The maximum adsorption capacity of biochar and biochar–MMT composite for CFX was  $122.16 \text{ mg g}^{-1}$  and  $167.36 \text{ mg g}^{-1}$ , respectively [30].

### Caffeine

CAF,  $C_8H_{10}N_4O_2$ , is a psychostimulant and analeptic compound. CAF is used in various medications, including pain relievers, antihistamines, diet tablets, and cold and flu medicines. Many adsorbents have been incorporated for their safe removal like biosorbents, activated carbons, graphene nanoplatelets, multi-walled CNTs, natural clays, hydrogels beads, and chitosan [132]. In a notable study [117], CAF was adsorbed to oxidized biochar derived from pine needles (PNCO). The pine needles were carbonized at  $650 \text{ }^\circ\text{C}$  and then oxidized using boiling nitric acid. The oxidation resulted in an adsorption capacity of  $1.41 \text{ mg g}^{-1}$  in real wastewater. Furthermore, Fourier transform infrared spectroscopy (FTIR) and ionic strength studies showed that the adsorption of CAF by PNCO is based on the formation of outer sphere complexes and electrostatic interactions (Fig. 6a) [117]. In another prominent example [96], MgAl-Layered double hydroxides–biochar composites were



**Fig. 6** Schematic representation of potential pathways of CPX adsorption onto the as prepared MSW–BC–MMT composite. Reproduced from with permission [30]. Copyright 2019, Elsevier Ltd



synthesized using bovine bone feedstock. The adsorption kinetics composite followed a PFO model suggesting physical adsorption. The equilibrium was attained within 20 min of contact time. Also, the RP model showed the best fit to the isotherm data, revealing the possibility of combined monolayer and multilayer processes. The composite showed an adsorption capacity of  $26.219 \text{ mg g}^{-1}$ , thus providing a better alternative to other treatment methods for the remediation of CAF laden aqueous matrix systems [96].

### Sodium diclofenac

SD,  $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NNaO}_2$ , is one of the extensively used NSAID drugs, widely applied to treat livestock in developing countries, with an estimated 940 tons per year consumption [118]. A wide variety of adsorbents have been tested for SD removal. Notably, the adsorption of SD on biochar derived from rice hulls provided up to 96% removal. The feedstock was torrefied at  $350 \text{ }^\circ\text{C}$  for 1 h. As revealed by FTIR analysis of biochar, the presence of  $\text{C}=\text{O}$  and other carbonyl or carboxyl groups provided significant sites for adsorption [118]. Another attractive strategy for SD removal is the use of acid-activated biochar. To this end, biochar derived from moringa seeds powder was further activated by  $\text{H}_3\text{PO}_4$  at  $450 \text{ }^\circ\text{C}$ , with a residence time of 2 h and a temperature gradient of  $10 \text{ }^\circ\text{C min}^{-1}$ . This resulted in a multifold increase in adsorption capacity of up to  $100.876 \text{ mg}$  of SD per gram of the as-synthesized biochar [27].

### Ofloxacin

OFL,  $\text{C}_{18}\text{H}_{20}\text{FN}_3\text{O}_4$ , is a fluoroquinolones drug, which is used as an antibiotic. Substantial traces of OFL in surface water have been reported. Pristine and engineered biochar, like magnetic biochar, have been used to remove OFL in aqueous matrices. As a prominent example, magnetic biochar prepared from the sludge of a textile effluent treatment plant at  $400 \text{ }^\circ\text{C}$  for 4 h at a thermal gradient of  $10 \text{ }^\circ\text{C min}^{-1}$  successfully removed OFL from an aqueous solution with a removal efficiency of 96%. The feedstock sludge had a predominance of iron chloride, rendering magnetic characteristics to the biochar. At optimum parameters, i.e., biochar dose of  $5 \text{ g L}^{-1}$ , temperature of  $25 \text{ }^\circ\text{C}$ , pH of 6, and contact time of 5 h, the magnetic biochar showed an adsorption capacity of  $19.7 \text{ mg g}^{-1}$  for OFL in the aqueous matrix [99].

### Ibuprofen

IBP,  $\text{C}_{13}\text{H}_{18}\text{O}_2$ , is an NSAID, antipyretic and analgesic drug. Biochar from various lignocellulose feedstocks like coconut shell [22], date stone seeds [88], wood apple (*Aegle marmelos*) fruit shell [24], wood chips [23], and mung bean husk [119] have been effectively used in the adsorption of IBP

from the aqueous matrices. Notably, biochar synthesized from mung bean husk at  $550 \text{ }^\circ\text{C}$  for 1 h at a heating rate of  $55 \text{ }^\circ\text{C per 15 min}$ , followed by steam activated at  $650 \text{ }^\circ\text{C}$ , showed 99% IBP removal. This removal efficiency was achieved at an optimized adsorbent dose of  $0.1 \text{ g L}^{-1}$ , IBP initial concentration of  $20 \text{ mg L}^{-1}$ , contact time of 120 min, agitation speed of 200 rpm, pH of 2, and temperature of  $20 \text{ }^\circ\text{C}$  [119]. Similarly, biochar derived from date stone at  $700 \text{ }^\circ\text{C}$  was activated with steam (DSPB) and chemically by  $\text{H}_3\text{PO}_4$  (DSCC). These activations resulted in different SSAs, such as  $513 \text{ m}^2 \text{ g}^{-1}$  for DSPB and  $342 \text{ m}^2 \text{ g}^{-1}$  for DSCC. Furthermore, this impacted the IBP adsorption performance, as 96% was removed by DSPB after a contact time of 18 h and 87% by DSCC after 21 h [88]. The elimination mechanism relied mostly on the creation of electrostatic and  $\pi$ - $\pi$  interactions, depicted in Fig. 6b. Similarly, physically and chemically activated biochar derived from coconut shells showed an IBP removal percentages of 73.71% and 80.37%, respectively [22].

### Tetracycline

TC,  $\text{C}_{22}\text{H}_{24}\text{O}_8\text{N}_2$ , is one of the most widely consumed antibiotics due to its broad-spectrum application and low cost. TC removal via adsorption has been successfully achieved by researchers using biochar. Most of the biochar subjected to TC removal is typically synthesized at pyrolytic temperatures above  $500 \text{ }^\circ\text{C}$  using various plant-derived biomass and animal manure like rice straw and swine manure [120], MSW [121], food and garden waste [92], and rice straw [122], among others. In an investigation studying the effect of pyrolytic temperatures on the biochar efficiency for TC adsorption, rice straw was subjected to temperatures of  $500 \text{ }^\circ\text{C}$  and  $700 \text{ }^\circ\text{C}$  for 2 h at a heating rate of  $26 \text{ }^\circ\text{C min}^{-1}$ . The biochar synthesized at  $700 \text{ }^\circ\text{C}$  provided a higher adsorption capacity and removal efficiency of 96.7%, attributed to relatively high SSA and  $\pi$ - $\pi$  electron donor-acceptor interactions with the biochar surface. Furthermore, the removal mechanism mainly involved hydrogen bonding and electrostatic interactions (Fig. 6c) [122]. Moreover, biochar-clay composites have also been successfully tested for the adsorptive removal of TC. The biochar-clay composite synthesized from MMT clay and pre-treated MSW, via pyrolysis at  $500 \text{ }^\circ\text{C}$  for 30 min showed significant TC adsorption capacity in the pH range of 3.0–9.0. The adsorption data best fit the Freundlich model, indicating multilayer adsorption. The presence of high surface activity, greater surface area, and interlayer spaces provided by the layered MMT clay mineral, improved the TC adsorption capacity of MSW-MMT composite via both surface adsorption and intercalation interactions [121]. Pristine biochar derived from food and garden waste showed an adsorption capacity of  $9.45 \text{ mg g}^{-1}$  for TC adsorption at neutral pH, using an adsorbent dose of  $2 \text{ g L}^{-1}$  for a contact time of 12 h. The biochar was synthesized via pyrolysis in a

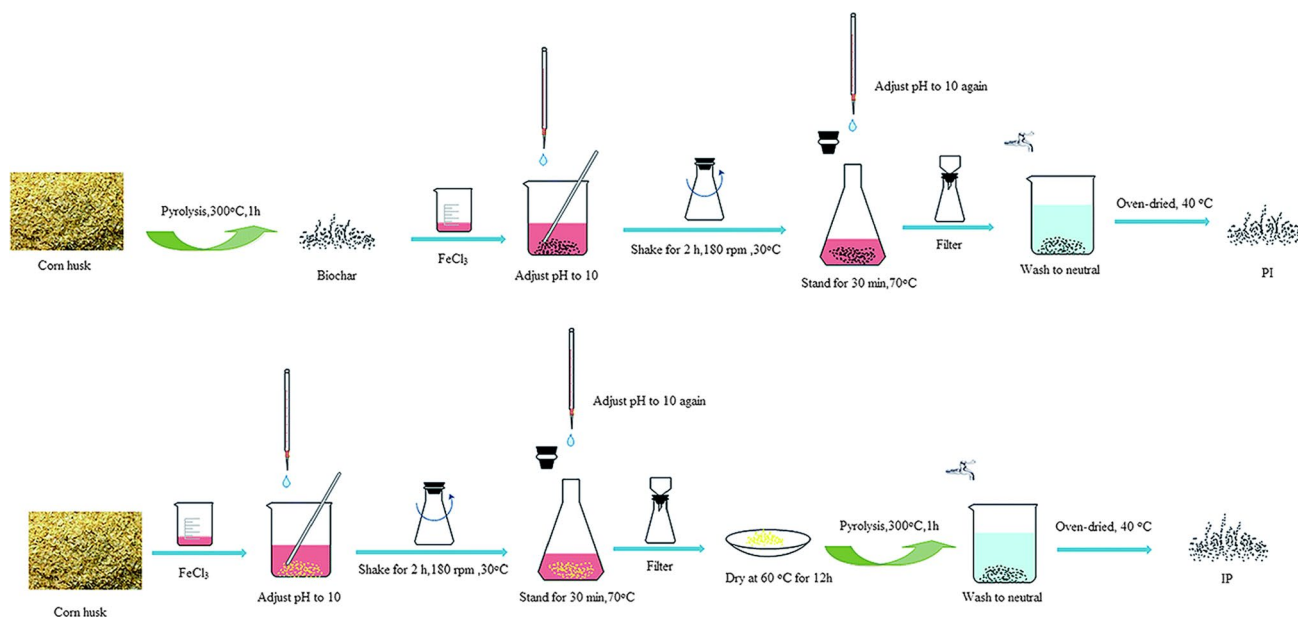
novel heat pipe reactor at 300 °C for 12 h. The as-synthesized biochar showed the presence of oxygen and hydrogen containing functional groups, making interaction possible with –OH groups present on TC molecules [92]. Furthermore, chemically activated biochar derived from rice straw and swine manure, pyrolyzed under identical conditions, resulted in varying SSAs, which affected the TC adsorption capacity. The TC adsorption capacity was also significantly enhanced by increasing the pH from 5.0 to 9.0 [120].

In another study [26], the adsorption of salicylic acid (SA), NPX, and KETO onto Fe<sub>2</sub>O<sub>3</sub>-impregnated biochar, derived from walnut shell biomass at 600 °C for 2 h, was carried out in an ultrasound bath. The adsorption was higher in the acidic medium than in the basic medium, with maximum adsorption capacities reaching 683, 533, and 444 mg g<sup>-1</sup> for SA, NPX, and KETO, respectively. The PSO model and Langmuir model fitted well with the experimental adsorption kinetics and isotherm data, respectively, emphasizing the process being predominantly physisorption, involving hydrogen bonds,  $\pi$ – $\pi$  interactions, and electrostatic attraction, owing to the presence of surface functional groups.

## Levofloxacin

LEV, C<sub>18</sub>H<sub>20</sub>FN<sub>3</sub>O<sub>4</sub>, is widely used to treat mild-to-moderate respiratory and urinary tract infections and thus often ends up in various aqueous matrices. Biochar has

shown promising results in the adsorption removal of LEV. Notably, biochar composites synthesized from corn husks with and without the impregnation of iron oxide were used for the adsorption of LEV. The as-synthesized biochar involved the adsorption of LEV through  $\pi$ – $\pi$  interactions, hydrogen bonds, and electrostatic attraction (Fig. 6d). The feedstock was subjected to a temperature of 300 °C for 1 h at a thermal gradient of 5 °C min<sup>-1</sup>, with iron oxides impregnated before pyrolysis (IP-BCFe) and after pyrolysis (PI-BCFe) (Fig. 7). The pre- and post-iron oxide treatments resulted in compositional and characteristic differences in the two biochar. PI-BCFe composite had a lower surface area of 94.9 mg g<sup>-1</sup> and less iron content; however, it showed a higher adsorption capacity of 273.7 mg g<sup>-1</sup>. This higher adsorption capacity adhered to the presence of multiple hydroxyl moieties in PI-BCFe, which participated in the hydrogen bonding, complexation, and replacement of Fe with –OH groups in LEV adsorption [35]. The function of iron impregnation can be compared to a prior study [36], in which LEV adsorption was much lower. The biochar was derived from two different feedstocks, pine wood chips and rice husk, at a temperature of 600 °C for 2 h, with a temperature gradient of 10 °C min<sup>-1</sup>. These pristine biochar showed adsorption capacities of 7.72 mg g<sup>-1</sup> and 4.99 mg g<sup>-1</sup>, respectively, which are many folds less than the adsorption capacity of iron-impregnated biochar (PI-BCFe) [36].



**Fig. 7** Steps for the synthesis of pyrolysis–impregnation biochar (PI-BCFe) and impregnation–pyrolysis biochar (IP-BCFe) derived from corn husk. Reproduced with permission [35]. Copyright 2019, Royal Society of Chemistry

## Conclusions and outlook

This article reviews the latest progress on biochar-based adsorption removal of PCs from aqueous environment. Additionally, this article attempts to address different adsorption routes and theoretical kinetic models available to design efficient treatment process for different classes of PCs, viz., antibiotics, analgesics, NSAIDs, salicylates, antibacterials, and anti-infectives. Clearly, biochar facilitates PCs removal via  $\pi$ - $\pi$  interactions among  $\pi$  electrons of biochar and aromatic portion of the PCs, the formation of hydrogen bonds between surface hydrogen on biochar and more electronegative functional groups present on the surface of the PCs for further adsorption. Physicochemical properties like SSA and surface charge govern adsorption by pore entrapment and electrostatic interactions, respectively. Further, the pH of the system governs the surface charge of the biochar and speciation of the target PCs.

PCs are persistent and recalcitrant components present in every matrix of the aquatic environment. The fate and transport of each type of PCs poses different environmental impacts. The transformed metabolites are even more dangerous and poisonous than their original form. Therefore, adverse effects on environment are common if the residual PCs are continuously released in the environment, mostly in the aqueous matrix. The fate and transport of the disposed pharmaceutical and clinical drugs occur in the environment and disturb the whole ecosystem. Different methods are formulated worldwide to treat and remove PCs from the surface water, groundwater, and other water matrices, including physicochemical and biological methods such as biodegradation, ASP, constructed wetlands, photodegradation, electrocoagulation, membrane separation, and AOPs. Most of these methods show moderate-to-excellent performance in eliminating PCs from wastewater. Evolution of toxic end products via aforementioned methods provides a way to explore adsorption as a favorable and common approach. As a result, a variety of conventional adsorbents have been investigated and their removal efficiency has been well documented in the scientific literature. However, in recent years, the ultimate goal for ensuring cost effective and sustainable removal of PCs warrants inexpensive adsorbents, such as biochar derived from renewable biomass feedstocks. It is evident from the breadth of the discussion in this review that biochar has enormous potential for eliminating PCs from wastewater. Additionally, new drugs are added to pharmaceutical market with each passing day. Therefore, it is necessary to fill the research gaps and to expand the existing knowledge of biochar-PCs interaction mechanism and removal efficiencies,

which will promote the practical applications of biochar in actual wastewater treatment systems. The process for activation, modification, and engineering of biochar materials into high-end advanced pharmaceutical adsorbents is well suited for the diverse chemical nature of futuristic PCs and their easy adsorption. Regardless of the amazing properties of biochar, the possible negative effects of long-term use of biochar also need to be studied. The stability of biochar can be a matter of concern for long-term use in wastewater systems. In particular, the release of carbon due to instability in degree of aromatic condensation of biochar may add to the carbon content in the effluent. This may have adverse effects on the degradation of PCs and may create more toxic byproducts. Furthermore, leaching of heavy metals may also occur in case of biochar derived from sludges. The stability of biochar is greatly defined by two parameters, viz., the choice of feedstock and the conditions during thermal treatment. Thus, these parameters must be correlated for synthesis of stable biochar for long-term usage. Overall, the efficiency to remove PCs from aqueous solutions by various biochar at the lab scale has been widely reported. However, their efficiency in real effluents with notable concentrations of PCs and suitability in handling large volumes of effluents should be investigated. Further, the regeneration and stability of biochar over several adsorption cycles should be examined.

According to the current status of the research, some of the recommendations for further advancement in the removal of PCs with the aid of biochar are as follows:

- A legal framework of standard protocols or guidelines on a global platform should be developed that will direct pharmacists and the general public to deal with the various classes of PCs within permissible limits.
- Pilot-scale-based research must be conducted to determine the on-site application of biochar-mediated adsorption technologies for the efficient removal of PCs from WWTPs.
- The optimization of pyrolysis parameters for biochar synthesis will facilitate their large-scale production.
- The stability and leachability of biochar-based adsorbents must be thoroughly examined. This, in turn, will facilitate the practical utility of the material.
- Biochar has the potential to remove other pollutants in aquatic ecosystems, such as nitrogen and phosphorous compounds, which are the major causative agents of eutrophication. Therefore, the rational modification of biochar would facilitate the simultaneous removal of multiple pollutants from aqueous matrices.

## Declarations

**Conflicts of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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