

Sorptive removal of pharmaceutical and personal care products from water and wastewater

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9.1 Introduction

Pharmaceutical and personal care products (PPCPs) comprise a diverse group of organic chemicals including therapeutic drugs, veterinary drugs, fragrances, cosmetics, diagnostic agents, surfactants, and nutraceuticals. Pharmaceuticals are used to prevent or treat human and animal diseases, while personal care products are used for personal hygiene to improve the quality of daily life. PPCPs are bioactive complex molecules as they can exist as neutral, anionic, cationic, or zwitterionic molecules depending on the environmental conditions and octanol/water partition coefficient (K_{ow}) values (Kümmerer, 2008). Also, their specific properties, such as solubility, polarity, acid dissociation constants (pKa values), hydrophobicity and hydrophilicity, K_{ow} , and the distribution coefficient (K_D), are all pH dependent. These PPCPs and their bioactive metabolites have recently been recognized as emerging contaminants and are continually introduced into the environment mainly through untreated/treated sewage, livestock industries, human excretion, leeching from landfill, drain water, wastewater and sewage treatment plants, etc. (Daughton and Ternes, 1999).

In most of the countries, PPCPs are found in the environment due to the discharge of treated wastewater from wastewater treatment plants (WWTPs). Since the conventional wastewater treatment processes are not designed to remove PPCPs, those are found in subsequent discharge to surface waters including rivers, lakes, and coastal waters. It has been reported that more than 100 PPCPs have been reported in environmental waters (Ebele et al., 2017; Archer et al., 2017; Petrie et al., 2015). High concentrations of analgesic tramadol have been observed in river

water in the United Kingdom reaching the highest of 7731 ng/L (Kasprzyk-Hordern et al., 2009). The mostly reported PPCPs are nonsteroidal antiinflammatory drugs (NSAIDs), β -blockers, antidepressants, and the antiepileptic carbamazepine (Petrie et al., 2015). Those have been categorized as highly prescribed (>1000 kg per annum) drugs and hence ubiquitous to influent wastewaters. At the same time, antimicrobials, sunscreen agents, and preservatives are also considered as high usage PPCPs (Petrie et al., 2015). As an example, the sunscreen agent 4-benzophenone has been observed at concentrations as high as 5800 ng/L (Kasprzyk-Hordern et al., 2009).

The presence of high levels of diclofenac, ibuprofen, ketoprofen, sulfamethoxazole (SMX), and bezafibrate was observed in South African surface waters (Agunbiade and Moodley, 2016). A most recent publication from South Africa further reveals the presence of antibiotics, NSAIDs, lipid regulators, antihistamines, X-ray contrast media, beta blockers, stimulants, antidepressants, medications to hypertension, antiepileptic, diabetes, and analgesics in the downstream treated wastewaters in high concentrations (Archer et al., 2017). A clear view of the concentrations of different classes of PPCPs in the freshwater aquatic environment was well reported from each continent in the study by Ebele et al. (2017). Based on country-wise data the highest concentrations of NSAIDs were reported from Nigeria and India, respectively (Ebele et al., 2017). Other than waters, soil can be also one of the sinks for PPCPs. The presence of PPCPs in environmental matrices may adversely influence the biota due to their persistence, bioaccumulation, and toxicity. The effects have been listed well in different studies (Archer et al., 2017; Ebele et al., 2017).

Recently, numerous biological, chemical, and physical approaches have been studied for the remediation of PPCP contaminated sites. Among other techniques available such as membrane/electrochemical separation technologies, bioremediation, ozonation, coagulation, volatilization, and sedimentation, sorption-based techniques have been recently recognized as a friendly approach to remove PPCPs from aqueous solutions (Xu et al., 2017). The activated sludge system is the most common conventional biological treatment process adopted in the WWTPs. It has the capacity to remove the PPCPs from the wastewater; however, the removal efficiency changed greatly and varied with the physicochemical properties of compounds as well as environmental conditions and operational parameters (Wang and Wang, 2016). Removal efficiencies have been well listed with different treatment processes of the WWTPs indicated the diversity of PPCPs removal based on the types (Wang and Wang, 2016). Other than conventional processes of WWTPs, Fenton oxidation, ultra violet (UV) treatment, ozone degradation, microbial degradation, adsorption, irradiation, and integrated techniques, are used for the removal of PPCPs from environmental waters. The development of cheaper and effective sorbents is essential for the removal of PPCPs; however, it is still a challenge due to their complex chemical nature. In order to enhance the sorptive removal capacity for PPCPs, different adsorbents have been researched and modified for the removal of PPCPs from aqueous media. This chapter provides a comprehensive overview of sorptive removal techniques of PPCPs and the mechanism of interactions.

9.2 Technologies available for pharmaceutical and personal care products removal

A variety of technologies such as membrane/electrochemical separation technologies, biological processes, ozonation, and physicochemical treatments including coagulation, volatilization, sorption, and sedimentation have been employed for the removal of PPCPs from water and wastewater. The application of these diverse techniques would depend on the contaminant level, cost of the process, and chemical nature of PPCPs.

A number of separation processes such as microseparation, nanofiltration, and ultrafiltration are recommended for the contaminant removal in aqueous media. However, the efficiencies of removing PPCPs by separation processes are markedly dependent on the size and molecular weight of the target PPCP molecules. [Nghiem et al. \(2004\)](#) suggested that hormones removal by nanomembranes could depend on the size of the hormone molecule, hydrogen bonding of hormones to membrane functional groups, and hydrophobic interactions of the hormone with the membrane matrix. The nanofiltration membrane with charged surface modifying macromolecule exhibited long-term performance in separating ibuprofen molecule in aqueous media ([Rana et al., 2012](#)). Also, it has been reported that steroid hormones can adsorb onto membranes via hydrogen bonding and hydrophobic interactions with membrane polymer ([Schäfer et al., 2003](#)).

Electrochemical separation technologies such as electrocoagulation, internal microelectrolysis are cable of isolating only the pollutants from water, whereas other electrochemical advanced electrochemical processes such as anodic oxidation, electrooxidation, electro-Fenton reactions, photoelectro-Fenton, and photoelectrocatalysis remediate contaminated water by degradation of pharmaceuticals ([Sirés and Brillas, 2012](#)). The use and performance of different electrochemical advanced oxidation processes for the treatments of PPCPs have been extensively studied ([Feng et al., 2010](#); [Murugananthan et al., 2010](#); [Boudreau et al., 2010](#); [Zhao et al., 2009](#)). These methods were effective in degradation of PPCPs in aqueous media. However, electrochemical degradation processes can produce more toxic and biorecalcitrant by-products than the parent PPCPs ([Sirés and Brillas, 2012](#)).

The ozonation process is considered as another promising technology for the treatment of PPCPs contaminated water ([Esplugas et al., 2007](#); [Ek et al., 2014](#)). The complete removal of carbamazepine in natural water was observed by the ozonation process ([Andreozzi et al., 2002](#)). It was observed complete removal of paracetamol with 30% mineralization after ozonation process. Oxalic, glyoxylic, cetomalonic, and formic acids, and hydroquinone were formed as intermediate products ([Andreozzi et al., 2003](#)). Even though ozone treatment processes have been applied with success, it is crucial to know the toxicity of intermediate compounds that are formed after ozonation process.

Biological treatments are relatively new approaches to remove and degrade PPCPs in aqueous media. Fungi use their extracellular enzymes to break down many stable compounds ([Ek et al., 2014](#)). [Rodarte-Morales et al. \(2011\)](#)

investigated the application of three different fungi for the removal of PPCPs belonging to different therapeutic groups: antidepressants (citalopram and fluoxetine), antibiotics (SMX), antiinflammatory drugs (diclofenac, ibuprofen, and naproxen), antiepileptics (carbamazepine), tranquilizers (diazepam), and fragrances (celestolide, galaxolide, and tonalide). Complete degradation of all the PPCPs except for fluoxetine and diazepam was observed; however, the implementation of these biological techniques in real environmental conditions should be further studied.

Sorption-based techniques are considered as a friendly approach to remove PPCPs because of their simplicity of design, low initial cost, and ease of operation (Xu et al., 2017). However, proper disposal/regeneration of sorbents needs to be considered when recommending sorption-based techniques for long-term applications. The sorbents used for PPCPs removal and detailed mechanisms of actions will be discussed in detail in the following sections.

9.3 Pharmaceutical and personal care products removal using commercial activated carbons

In general, the high efficiency of adsorption on commercial activated carbon (CAC) for the removal of wide varieties of organic and inorganic contaminants from aqueous media has made it an ideal alternative to other techniques. CACs have been extensively used for PPCPs removal from aqueous media (Yoon et al., 2003; Tsai et al., 2006; Mestre et al., 2007). Yoon et al. (2003) showed that the application of CAC was feasible for >99% removal of three estrogenic compounds [bisphenol A (BPA), 17 β -estradiol, and 17 α -ethynyl] from raw drinking waters. The chemical properties of PPCPs such as pKa, log K_{ow} values had significant effect on sorption efficiencies, and the highest removal capacities corresponded to largest log K_{ow} values (Yoon et al., 2003). Also, the properties of CAC materials affected PPCPs removal efficiencies. Most PPCPs become ionizable depending on solution pH. Further, the surface of the CAC is positively/negatively/neutral charged depending on solution pH and point of zero charge (pzc) (pH_{pzc}) values of CAC materials. For example, CAC surface is negatively charged at basic solution pH ($pH > pzc$ of CAC), and ionizable PPCP molecules [e.g., tetracyclines (TCs), sulfonamides] are in negatively charged form. In this scenario, electrostatic repulsive forces would dominate between anionic PPCPs molecules and CAC surfaces (Teixidó et al., 2011).

The porous nature of CAC gives them a large surface area and therefore increases in PPCPs sorption capacities. An activated carbon prepared from agricultural by-product olive waste cakes was studied for potential removal of ibuprofen, ketoprofen, naproxen, and diclofenac in aqueous media (Baccar et al., 2012).

Although CACs have been recognized as a preferred sorbent for PPCPs removal, its widespread use is limited due to its several drawbacks. Preparation process is costly and requires an additional effort on the activation process. The regeneration

of activated carbon is challenging, and production process needs high temperature and pressure conditions (Le Noir et al., 2009). Also, it has drawback in the removal of competitive interfering compounds (Dai et al., 2012). Therefore alternative non-conventional sorbents having selective removal abilities of contaminants and lesser production costs have been introduced as inexpensive sorbents.

9.4 Nonconventional low-cost sorbents for the removal of pharmaceutical and personal care products

Recent attention has paid to develop nonconventional sorbents due to their lesser manufacturing cost and high availability (Dai et al., 2012). Agriculture solid wastes, industrial by-products, natural clay minerals, biosorbents, and some synthetic sorbents have been widely used as nonconventional low-cost sorbents.

9.4.1 Agricultural solid waste

Agricultural solid waste is a readily available, renewable, and low-cost raw material. Agriculture being of high economic importance for the developing countries throughout the world, contribution to accelerated amounts of agricultural waste load every year increments (Abioye and Ani, 2015). The utilization of these solid wastes from agriculture fulfills two main aspects as it helps to diminish waste load and is involved to produce economically valuable products (Kulkarni, 2014; Kulkarni et al., 2015; Ramachandran et al., 2014). Table 9.1 shows the different types of agricultural wastes used in the removal of some commonly used antibiotics and pharmaceutical ingredient.

Agricultural wastes are predominantly composed with cellulose, although hemicellulose, lignin, lipids, proteins, starch, and simple sugar species also serve as structural components. A variety of functional groups associated with these constituents possess a capability to remove diverse range of contaminants making complexes with them (Sud et al., 2008).

Past studies have shown the capacity of adsorbents generated from different types of agricultural solid wastes such as rice husk (Vadivelan and Kumar, 2005), coconut waste (Hameed et al., 2008), sawdust, and other wood type materials (Aydin et al., 2004; Shukla et al., 2002) such as jackfruit peel (Hameed, 2009), shells of almond and hazelnut, and peel of orange (Arami et al., 2005) to remove organic pollutants including PPCPs.

Husk of the grains, including rice husk and wheat husk, has high capacity to generate economically feasible adsorbents hence it has high production rates as an agricultural by-product in most developing countries. Chen et al. (2016) investigated about the adsorption capacity of TC onto rice husk and found out 8.37 mg/g of adsorption which is comparatively high value that has been reported for most of the other adsorbent materials in literature. Furthermore the study that has done by

Table 9.1 Agricultural wastes used for commonly used pharmaceutical ingredient

| Adsorbent | Pharmaceutical ingredient | Dosage (mg/L) | pH | Adsorption capacity (mg/g) | Isotherm | References |
|-------------------------------|----------------------------------|----------------------|-----------|-----------------------------------|-----------------|--|
| Bamboo waste activated carbon | Ibuprofen | 2.0 | 5.0 | 278.55 | Langmuir | Reza et al. (2014) |
| Rice husk biochar | Tetracycline | 1.0 | 2.0 | | | Jing et al. (2014) |
| Rice straw | Clofibric acid | 1.0 | 2.0 | 126.30 | Freundlich | Liu et al. (2013) |
| Pomegranate wood-AC | Amoxicillin | 0.8 | 6.0 | 437.00 | Langmuir | Moussavi et al. (2013) |

Tanin and Gurgey (1988) explained the water purification ability of the carbon which made from rice husk.

Tree bark, a by-product from timber industry, contains higher amounts of tannin and identified as a potential adsorbent. The polyhydroxyl groups associated with the tannin act as the active part of the molecules for adsorption process (Ali et al., 2012). Pouretedal and Sadegh (2014) has been assessed the efficiency of activated carbon nanoparticles generated from vine wood for the removal of few antibiotics, namely, amoxicillin, cephalixin, TC, and penicillin G. The results of that study have shown highest antibiotics removal of 0.4 g/L at pH 2 with the adsorbent which they prepared, and it has abilities to compete with other carbon adsorbents namely graphite, graphene, and nanotubes.

El-Shafey et al. (2012) carried out a study to remove ciprofloxacin from aqueous media by chemically preparing carbon from date palm (*Phoenix dactylifera*) an important commercial crop especially in Oman and Gulf states which caused to produce large amount of waste leaflets (i.e., 180,000 and 3 million tons, respectively) in every year (Al-Yahyai and Al-Khanjari, 2008). In this study the carbon adsorbent were prepared by sulfuric acid carbonization of date palm leaves at 160°C. During the study the highest adsorption capacities of Ciprofloxacin were achieved at initial pH 6, and wet adsorbent showed high performance than dry adsorbent. This study suggests that the adsorption mechanism for Ciprofloxacin is physical, spontaneous, and endothermic and the adsorption is primarily occurred presumably by cation exchange and hydrogen bonding.

Villaescusa et al. (2011) investigated about three agricultural wastes: grape stalk, yohimbe bark, and cork bark for the removal of paracetamol. The adsorbents were prepared by drying the feedstock at 110°C for constant weight and finally obtained the 0.63–0.75 mm of particle size. Among all the three adsorbents, the grape stalk waste showed the highest adsorbent capacity for paracetamol removal. Sorption study showed that the mechanism was not pH dependent, suggesting that the adsorption is not occurred by the ion exchange. Modeling calculations reflects that the π -stacking interactions among the lignin syringyl and guaiacyl moieties in grape stalk and the aromatic ring in paracetamol together with H-bonding accountable for the sorption of paracetamol.

9.4.2 Industrial by-products

Developing industrial activities are generating accelerated quantities of by-products (Bhatnagar and Minocha, 2006). These by-products including fly ash, sludge, and red mud are readily available with virtually no cost and can be utilized to make low-cost adsorbents to treat waste and wastewater (Grassi et al., 2012).

Fly ash is the major by-product that results from the coal-based thermal power plants and has increasing production rates particularly due to the increasing demand for electricity. It is originated from noncombustible residue carried among the flue gas and characterized by uniformly distributed fine particles, ranging from 1 to 10 μm of diameter (Bhatnagar and Minocha, 2006). Elevated quantities of silica and alumina present in fly ash make it a good adsorbent, and elevated production

rates enable the bulk use of it. [Aksu and Yener \(1999\)](#) found that a reasonable adsorptive capacity of fly ash for phenolic compounds and the maximum adsorption value has been reported as 27.9 mg/g.

Blast furnace slag is a type of industrial solid waste particularly originated from steel industry. Although it has been generated problems in disposal, it can convert to be an economically feasible adsorbent. Previous studies revealed the effectiveness of it for the removal dye contaminants in wastewater ([Ali et al., 2012](#)). [Gupta et al. \(1990\)](#) proved the efficiency of industrial slag produced from iron and steel company for the removal of malachite green dye from an aqueous system. That study was able to be achieved 99.9% of dye removal at lower concentrations.

Different types of solid waste originated from petroleum refineries have been tested to produce adsorbents by several studies. Here, the solid wastes were converted into activated carbon in order to use as an absorbent. The study done by [Fasoli and Genon \(1976\)](#) was involved to develop granular carbon from refinery wastes to treat insoluble oil splits in wastewater. The study used spent sand filter as precursor to produce granular carbon.

Therefore, it is evident the capability of industrial solid wastes can be an effective adsorbents to remove organic contaminants say PPCPs from waste and wastewater.

9.4.3 Natural clay minerals

There have been numerous efforts by different environmentalist to remove aqueous contaminants such as the PPCP using developed natural clay-based sorbents. The dynamics of how the pharmaceutically active ingredient reacts with the mineral phases in the environment is an active study to understand its presence in the ecosystem ([Thiebault et al., 2016](#)). It is due the minerals' large surface area and high cation exchange capacity, they have been exploited as sorbents for both organic and inorganic pollutants. The removal of six widely used pharmaceuticals was studied to see the adsorption nature of clays: ibuprofen, diclofenac, ketoprofen, carbamazepine, BPA, and a bactericidal agent, triclosan. Majority of these pharmaceuticals chemicals are highly dependent on the acidity that they exist and they vary at different solution conditions. This changes the mechanism of adsorption onto the structured clays as long as the fluctuating pH nature persists ([Styszko et al., 2015](#)). The interactions of pharmaceutical active compound or PPCP's on montmorillonite and kaolinite are the most common clay for the treatment as these are the most abundant ([Tsai et al., 2016](#)). Both have a slate-like structure that can retain the active molecules not only on the surfaces of the layers but the interlayers as well.

9.4.3.1 Palygorskite

Palygorskite is a magnesium–aluminum phyllosilicate with a fibrous structure that are being used as an adsorbents for PPCPs; its chain such as structure that can expand can restrict the entry of pharmaceutical active ingredient that is cation based from entering into the channels. This is what keeps it unique from the platy

minerals and can uptake cationic drug. Large specific surface area and high cation exchange capacity are two factors required for the removal of cationic pharmaceuticals. This silicate has already been rigorously studied for its use in heavy metal removal and dyes (Galan, 1996; Garcia Sanchez, 1999). Studies have proven for the removal of efficiency of TC (Chang et al., 2009). In Chang et al. (2009), sorption of TC on the mineral showed Langmuir isotherm with maximum of 99 mg/g of the palygorskite adsorbent at pH 8.7. The solution pH and the ionic strength had strong effects on the removal efficiency of TC uptake by palygorskite. The crystal lattice of the mineral structure was not changed as such because the adsorption was solely monolayer and on the external surface (Chang et al., 2009). Ranitidine (RT), inhibitors for gastric treatment, showed significant uptake by palygorskite using Langmuir isotherms, and the kinetics showed instantaneous RT removal and further unchanged crystal lattice structure confirming the monolayer adsorption instead of intercalation of RT between the layers (Li et al., 2016).

9.4.3.2 *Montmorillonite*

Montmorillonite belongs to the smectite family and is composed of two silica-based tetrahedral sheets with water molecules within the interlayer sheets and are easily available for the incoming contaminants. Organoclays are obtained when there is inorganic–organic ion exchange in the interlayers of the clays which can be proven as an effective adsorbate for organic and aromatic pollutants (Moore and Lockner, 2007).

TC is used as broad spectrum of antibiotics in human, animals, and in agriculture, and their adsorption on montmorillonite has been proven in many studies when it comes to its surface charge interaction between the adsorbate and the adsorbents (Browne et al., 1980; Parolo et al., 2008). Most of the mechanism postulates a cationic exchange–controlled process on the montmorillonite at relatively lower pH, and the intercalation between the interlayer spacing of the montmorillonite were speculated as well.

The removal of chlorpheniramine (CP), prominently used antihistamines in human and veterinary medicines, by Ca-montmorillonite was studied in Li et al. (2011). CP adsorption on clay made the slate structures between the clays to swell and have the molecule embedded within the spacing. The isotherm in this study showed a Langmuir fit with a capacity of over 0.72 mmol/g (Li et al., 2011).

9.4.4 *Biosorbents*

Biosorption is the use of biological material in order to remove pollutants which are particularly not easily biodegradable from solutions, and biosorbents are the biomaterials which are used in this process. Biosorbents include vast range of biomaterials including fungi, bacteria, algae as well as agricultural and industrial wastes. The major advantages of using biosorbents are mainly three fold: involves in situ remediation, no secondary contaminations, and inexpensive (Vijayaraghavan and Yun, 2008). For that reasons, they have been used as the most suitable substitute

over the commercially used adsorbents not only in pharmaceuticals removals from waters but also metals, dyes, and other organics.

The selection of the right sorbents involves solely on the physicochemical properties of the pharmaceutical active ingredient present. They are mostly driven by the hydrophobic interaction during the sorption process and the pH of the solvent as the speciation of these molecules in different aquatic environments has to be taken care of (Tadkaew et al., 2011). For instance, ibuprofen, ketoprofen, and diclofenac operate in acidic media rather than neutral as the hydrophobicity enhances at lower pH even lower than their acid dissociation values (pK_a) (Tadkaew et al., 2010, 2011; Urase et al., 2005).

In Ahsan et al. (2018), sulfonated saw dust (SD-SO₃H) was used as a cost-effective sorbents with a high efficiency proven for the removal of antibiotics such as TC, SMX, and certain endocrine-disruptive chemicals as BPA with an adsorption capacity as high as 290 mg/g. The structure of these molecules dissociated at an acidic pH predicting the interactions of the different species in the media due to the electrostatic interactions, for example, between the negatively charged SD-SO₃H and SMX⁺ species, and therefore the adsorption capacity decreases above a certain pH due to the enhanced electrostatic repulsion between the negatively charged SMX and the adsorbent (Ahsan et al., 2018).

Modifying the biosorbents to an active functional group for the adsorbate to cling on is an approach, and researchers take to increase further the efficiency of removal of the pharmaceutical active ingredients. NSAIDs acetaminophen and ibuprofen are being removed in one such approach using saccharides-based chitin modified with lignin (Żółtowska-Aksamitowska et al., 2018).

9.4.5 Synthetic sorbents

Through the use of advanced materials for removing PPCPs from aquatic environments and also to maintain a relatively low operating conditions, cost-effective, and low energy usage, synthetic sorbents are now a technology that can eliminate the limitations other materials provide especially the porosity can be improved to provide for the adsorbents (Akhtar et al., 2016; Song and Jung, 2017). Carbonaceous adsorbents were the first sorbents for many applications and have purified harmful chemicals and metals; these include carbon materials, charcoal, activated sludge, biochar, and graphite. However, synthetic sorbents have got the noticeable advantage, compared to this commercially used material, which is their mechanical strength, and the larger surface area has proven promising. Its uniform size distribution and the capability to regenerate under mild conditions are the highlight for these synthetic sorbents which the natural organic matters do not provide. The inaccessible pores in the carbon-based sorbents make it a limitation over synthetic sorbents (De Ridder et al., 2012). Polymeric sorbents can be synthesized as ionic or hydrophobic that satisfies the removal of polar or nonpolar pharmaceuticals from water. They can be highly resistant to fouling and can last for over 2000 regeneration cycles (Akhtar et al., 2016; De Ridder et al., 2012).

Zeolites are microporous materials that have uniform pore distribution (structures in the form of networks of SiO_4 and AlO_4) and are used for water-treatment processes especially in the removal of organics due to large surfaces for adsorption, good as an ion exchanger, acid-based solid acid catalyst, and thermally stable and highly regenerative (Knappe et al., 2017). Although it has been proven as an enhanced material for adsorption, it is highly selective for a certain pollutants and solvents. Faujasite-type zeolites that are three-dimensional channel system with 12 membered rings are used for the removal of azithromycin, ofloxacin, and SMX antibiotics (De Sousa et al., 2018). The three antibiotics exhibited a pH dependency where the mechanism is as postulated above via electrostatic interactions and in addition to hydrogen bonding with varying physicochemical characteristics (De Sousa et al., 2018).

9.5 Biochar and engineered/design biochar for pharmaceutical and personal care products removal

Biochar, a stable carbon-rich by-product produced through pyrolysis/carbonization of biomass, has gained huge attention due to their various properties and application in different fields, including agricultural sector, energy production, climatic change mitigation as well as environmental remediation (Cha et al., 2016). Biochar was initially used as a soil amendment which may improve soil fertility, enhance agricultural productivity, increase soil nutrients and water holding capacity, and reduce emissions of other greenhouse gases (Woolf et al., 2010). Recently, it was used as an alternative low-cost adsorbent for the removal of a variety of organic contaminants including PPCPs from aqueous medium and soil (Han et al., 2013; Yang et al., 2016), due its high surface area, porosity, and high cation exchange capacity (Ahmad et al., 2014). Agricultural by-products and solid waste are mainly used as biomass resources. Biochar is generally produced via the thermal decomposition of biomass under a limited supply (or the absence) of oxygen (O_2) at 200°C – 900°C (Lehmann and Joseph, 2009).

In general physicochemical parameters of biochar (e.g., elemental composition, surface area, pore volume, pore size, distribution of pores, pH, and electrical conductivity) mainly depend upon feedstock type, pyrolysis temperature, heating rate, and residence time (Rajapaksha et al., 2016). Therefore adsorption capacity of biochar also varies with above factors.

Biochar produced by different feedstocks has been used as an adsorbent for the removal of PPCP from aqueous media. Pine wood biochar produced at 425°C exhibits low adsorption capacity for ibuprofen at high pH, because it presents as their carboxylate anions; hence negatively charged biochar surface results in electrostatic repulsion between adsorbent and adsorbate (Essandoh et al., 2015). Highest adsorption of ibuprofen was shown at intermediate pH (pH—8.0) via hydrogen bonds occurs between carboxylate anions and unionized surface phenolic groups present on biochar (Essandoh et al., 2015).

Adsorption efficiency of acetaminophen and naproxen by pine chip biochar produced at 300°C exceeded 90%, and adsorption efficiency of naproxen adsorption was comparatively higher than acetaminophen due to its high adsorption affinity (Jung et al., 2015). Polar π - π interactions dominated adsorption as well as π - π stacking, which is spread out more for naproxen because of its naphthalene aromatic ring compared to benzene ring in acetaminophen. All the biochars produced at 450°C and 600°C using bamboo, Brazilian pepper wood, sugarcane bagasse, and hickory wood exhibited certain potential to remove SMX; lowest sorption ability was obtained for hickory wood biochar produced at 450°C and highest sorption was showed by sugarcane bagasse biochar produced at 450°C and 600°C (Yao et al., 2012b). Except hickory wood biochar produced at 450°C, all the other biochars produced at 450°C were shown higher adsorption ability compared to biochar produced at 600°C, because biochar produced at high pyrolysis temperature may consist of few functional groups contrast to biochar produced at low pyrolysis temperature (Gaskin et al., 2008; Mukherjee et al., 2011). Therefore higher adsorption at low pyrolysis temperature suggested that surface functional groups play the major role in adsorption than surface area or hydrophobicity of biochar (Yao et al., 2012b). Biochar prepared by giant reed material feedstock was also shown similar trend, and in this scenario, the adsorption of SMX was pH dependent (Zheng et al., 2013). However, according to Li et al. (2017a) and Wang et al. (2017), the adsorption capacities of cow manure and rice husk-derived biochar for oxytetracycline and TC were increased for respective antibiotics with the increase of pyrolysis temperature. This suggests that surface area played the main role during adsorption, not the surface functional groups available on biochar. Both oxytetracycline and TC adsorption were dominated by π - π electron-donor-acceptor (EDA) interactions (Wang et al., 2017; Li et al., 2017a).

Sludge samples were utilized for the production of biochars had high Brunauer-Emmett-Teller-specific surface areas and removed more than 80% of gatifloxacin from aqueous phase (Yao et al., 2012a). In addition biochar produced by utilizing number of biochars produced at different temperature was shown high removal efficiency of both florfenicol and ceftiofur. Among these, pine wood biochar produced at 550°C-650°C were exhibited up to 100% removal efficiency for florfenicol and ceftiofur (Mitchell et al., 2015).

Oxytetracycline antibiotic was effectively removed by biochar produced using maize straw and adsorption which was pH dependent. Cation exchange and π - π EDA interactions were the major mechanisms involved in adsorption (Jia et al., 2013).

9.5.1 Use of engineered design biochar for the removal of pharmaceutical and personal care product

For the purpose of further enhancement of adsorption capacities, an engineered biochar was prepared by different methods such as chemical modification, physical modification, impregnated with mineral sorbents, and magnetic modification

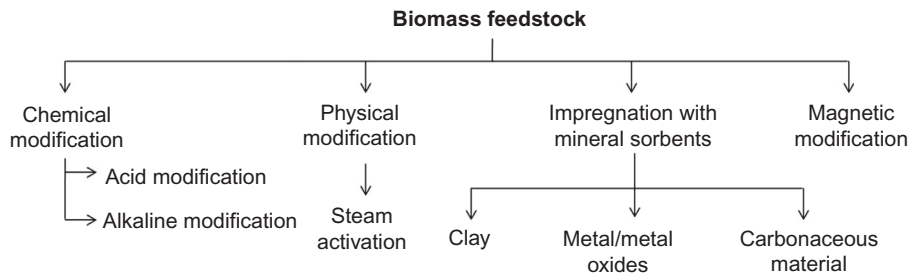


Figure 9.1 Major biochar modification methods.

(Rajapaksha et al., 2016; Ahmed et al., 2016). The abovementioned modification methods alter the physiochemical characteristics of biochars (Rajapaksha et al., 2016). In some instances, modification has caused negative impact on adsorption of relevant contaminant (Kim and Kan, 2016). Fig. 9.1 indicates the major modification methods available for the preparation of the engineered biochar.

Chemical modification of biochar is usually done via addition of acids or bases or intentional oxidation using hydrogen peroxide (H_2O_2), potassium permanganate (KMnO_4), ammonium persulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$], and ozone (O_3) which alters surface functional groups of biochar (Cho et al., 2010). Carbonization can be done simultaneously to activation or after activation (Qian et al., 2015). The enhancement of surface acidities and modification of porous structure of biochar resulted by acid activation (Lin et al., 2012). Most commonly used acids are phosphoric (H_3PO_4), sulfuric (H_2SO_4), nitric (HNO_3), and hydrochloric (HCl) acids (Rajapaksha et al., 2016). The H_2SO_4 , KOH , and methanol-modified biochars were shown in the enhanced TC removal. This enhancement of adsorption was observed due to $\pi-\pi$ EDA interactions occurred because of change of surface functional groups available in biochar (Ahmed et al., 2015). Adsorption affinity for SMX and TC of acid modified with HCl and Hydrofluoric acid (HF -treated) wheat straw and maize stalk biochar was higher than that of raw biochars (Ji et al., 2011). Major reason for above enhancement due to additional sites created on biochar surface results due to removal of minerals, mainly silicates (Ji et al., 2011).

Physical modification methods are cost-effective, however compared to chemically modified biochar efficiency is less. For the physical modification process, mainly oxidizing agents (CO_2), air, and steam are used (Rajapaksha et al., 2016). Through steam activation, activated biochar can be produced, and it has higher surface area (Rajapaksha et al., 2015). Steam activation significantly enhanced the sulfamethazine adsorption of burcucumber plants derived biochar and tea waste biochar compared to unmodified biochar (Rajapaksha et al., 2014, 2015). Electrostatic interactions, $\pi-\pi$ EDA interactions, hydrogen bonding as well as pore filling mechanisms involved in enhancement of adsorption of sulfamethazine, and at lower pH, $\pi-\pi$ EDA interactions become dominant (Ji et al., 2009).

The engineered biochar has been prepared via impregnating with mineral sorbents, including clays, metals, metal oxides, and carbonaceous materials.

Clay–biochar composites have been produced for the enhancement of adsorption capacity of biochar for certain contaminants (Yao et al., 2014). Even though several methods have been used for the production of clay–biochar composites, the most frequently used method is preparation of a clay–biochar slurry for pyrolysis (Yao et al., 2014; Fosso-Kankeu et al., 2015). Clay–biochar composite prepared by potato stem and natural attapulgite has shown higher adsorption capacity for norfloxacin in pH range of 2.0–11.0 (Li et al., 2017b). Major adsorption mechanisms involved were electrostatic attraction, hydrogen bonding formation, hydrophobic interaction, and π – π EDA interactions (Wang et al., 2013).

Biochar acts as a porous carbon platform for metal oxide upon which metal oxides precipitate and increase the surface area available for adsorption. Generally, impregnation with metal oxides is performed by soaking biochars or their feedstocks in solutions of metal nitrates or chlorides. The most frequently used impregnation agents described in the literature are FeCl_3 , Fe_2O_3 , $\text{Fe}(\text{NO}_3)_3$, and MgCl_2 (Frišták et al., 2017; Chaukura et al., 2017). Biochar was produced by combining agricultural waste with TiO_2 , which was shown higher adsorption capacity for SMX because of hydrophobic interactions occurred between modified biochar and antibiotic. However, it was lower compared to raw biochar due to availability of more carbon sites for π – π interaction between the antibiotic and biochar (Kim and Kan, 2016). Similarly, acid pretreated titanium dioxide (TiO_2) reed straw biochar composite and acid pretreated reed straw biochar were produced, and biochar surface and pores available on its surface were covered with TiO_2 . Therefore surface area of the biochar composite decreases, consequently reducing the adsorption capacity for SMX contrast to acid pretreated biochar. However, degradation of SMX was significantly higher compared to its degradation under simulated sunlight and UV light and then that achieved for pure TiO_2 (Zhang et al., 2017).

Biochar can be combined with carbonaceous materials which consist of functional groups capable of constructing strong bonds with both the biochar surface and the contaminant present in aqueous medium. Polysaccharides, amines, carbonaceous nanomaterials, and carbon nanotubes are the most commonly used agents (Zhou et al., 2013; Tang et al., 2015). Such modification can be achieved either through simple chemical reactions or by mixing biochar with polymers rich in amino groups such as polyethylenimine or chitosan (Zhou et al., 2013). Modification can further improve the adsorption capacities of biochars for different toxic pollutants.

Magnetic biochar was prepared for the improvement of separation of biochar after adsorption of relevant contaminant (Mohan et al., 2014; Wang et al., 2015). Magnetic particles are introduced onto biochar via chemical coprecipitation or pyrolysis activation; Fe, Fe_2O_3 , and Fe_3O_4 are the most commonly used ones (Zhu et al., 2014; Devi and Saroha, 2014). Magnetic biochar was prepared using coconut shell biochar combining with Fe_3O_4 for the sorptive removal of carbamazepine and TC. Magnetic modification has significantly increased the specific surface area, total pore volume, and micropore volume of biochar. Therefore adsorption

efficiency of carbamazepine and TC is high, because the adsorption mainly occurred on the biochar surfaces. In addition, reactive amide and hydroxyle groups [$-\text{CONH}_2$, $-\text{OH}$, and $-\text{N}(\text{CH}_3)_2$] present in above antibiotics may cause surface complexation with Fe_3O_4 . Further, small carbamazepine can diffuse more easily to pores available on biochar surface. Percentage removal of carbamazepine removal is stable throughout the pH range of 4.0–9.0, because it has neutral charge in above range (Rakshit et al., 2010), and no electrostatic interactions between negatively charged biochar surface and antibiotic. However, percentage removal of TC was decreased with the increase of pH due to its negative charge at high pH (pKa values of 3.3, 7.55, and 9.7) (Daghrir and Drogui, 2013). Relatively high magnetism of Fe_3O_4 (80 emu/g) (Xu et al., 2015) allows separation of magnetic biochar after the treatment. Magnetic carbon material was prepared by immersing hydrochar material in FeCl_3 solution and with the modification surface area, and pore volume has improved compared to raw material (Zhu et al., 2014).

9.5.2 Adsorption mechanisms of pharmaceutical and personal care products by biochar/engineered biochar

PPCPs are adsorbed onto the biochar and engineered biochar via both chemisorption and physisorption. In chemisorptions process, PPCPs are interacted with biochar surface via electrostatic interactions, ion exchange mechanisms, surface complexation $\pi-\pi$ EDA interactions, Van der Waals dispersion forces, and hydrogen bonding (Tables 9.2 and 9.3). Physisorption is occurred via pore filling mechanism and intercalation interactions.

At different pH, dominant form of antibiotics differs (Chang et al., 2014, 2016). Therefore adsorption of antibiotics onto the biochar and engineered biochar occurs via different mechanisms depending on the medium pH and pH_{pzc} of biochar (Fig. 9.2). Oxygen-containing functional groups are common on biochar produced at low pyrolysis temperatures which promote adsorption of PPCP via hydrogen bonding and surface complexation. However, the presence of large number of functional groups facilitates the development of larger water molecule clusters around them which create a stronger competition for the available surface area of biochar. Cationic organic contaminants exchange with cations present on biochar surface. The presence of swelling clays on biochar surface supports physical adsorption which occurred via intercalation interaction. Most of the pharmaceuticals consist of aromatic rings which interact with aromatic rings of biochar via $\pi-\pi$ EDA interactions. Metal and metal oxide modifications stimulate the adsorption of antibiotics through electrostatic interactions and surface complexation. Demineralization of biochar improves adsorption of antibiotic via pore filling mechanism due to creation of large number of extra micropores as a result of the removal of mineral components (Li et al., 2017a).

Table 9.2 Selected literature based on adsorption mechanisms involved in adsorption of pharmaceutical and personal care product onto pristine biochar

| Feedstock | Contaminant | Adsorption mechanisms | Reference |
|--|---|--|--|
| Pine wood | Ibuprofen | Van der Waals forces, permanent dipole–dipole attractions, π – π interactions and hydrogen bonding | Essandoh et al. (2015) |
| Pine wood | Acetaminophen and naproxen | π – π EDA interactions | Jung et al. (2015) |
| Agricultural wastes | Sulfamethoxazole | π – π EDA interactions | Kim and Kan (2016) |
| Bamboo, Brazilian pepper wood, sugarcane | Sulfamethoxazole | Hydrophobic interactions | Yao et al. (2012b) |
| Loblolly pine chips | Sulfamethoxazole, carbamazepine, and diclofenac | π – π EDA interactions, hydrogen bonding | Jung et al. (2013) |
| Bamboo biochar | Sulfamethazine, sulfamethoxazole, and sulfathiazole | Lewis acid–base interactions, π – π EDA interactions, hydrogen bonding | Ahmed et al. (2017) |
| Rice straw biochar | Sulfamethoxazole | π – π EDA interactions and surface complexation | Han et al. (2013) |
| Cow manure biochars | Oxytetracycline | π – π EDA interactions, pore-filling mechanism, and specific-site adsorption | Li et al. (2017a) |
| Rice husk | Tetracycline | π – π EDA interactions | Wang et al. (2017) |
| Maize straw | Oxytetracycline | Cation exchange and π – π EDA interactions | Jia et al. (2013) |

EDA, Electron–donor–acceptor.

Table 9.3 Selected literature based on adsorption mechanisms involved in adsorption of pharmaceutical and personal care product onto engineered biochar

| Feedstock | Modifier | Contaminant | Adsorption mechanisms | Reference |
|-----------------------------|--------------------------------|--------------------------------|--|--|
| Potato stem | Natural attapulgit | Norfloxacin | Electrostatic attraction, hydrogen bonding, hydrophobic interactions, and $\pi-\pi$ EDA interactions, intercalation interactions | Li et al. (2017b) |
| Wheat straw and maize stalk | HCl and HF | Sulfamethoxazole | Surface adsorption | Ji et al. (2011) |
| Burcucumber plant | Steam activated | Sulfamethazine | Electrostatic interactions, hydrophobic interactions, hydrogen bond, and $\pi-\pi$ EDA interactions | Rajapaksha et al. (2015) |
| Tea waste | Steam activated | Sulfamethazine | Electrostatic interactions, $\pi-\pi$ EDA interactions, hydrogen bonding, and pore-filling mechanisms | Rajapaksha et al. (2014) |
| Agricultural wastes | TiO ₂ | Sulfamethoxazole | Hydrophobic interactions and photocatalytic oxidation | Kim and Kan (2016) |
| Reed straw | TiO ₂ | Sulfamethoxazole | Photodegradation | Zhang et al. (2017) |
| Coconut shell | Fe ₃ O ₄ | Carbamazepine and tetracycline | Surface complexation and pore-filling mechanism | Shan et al. (2016) |

EDA, Electron–donor–acceptor; HCl, hydrochloric; TiO₂, titanium dioxide.

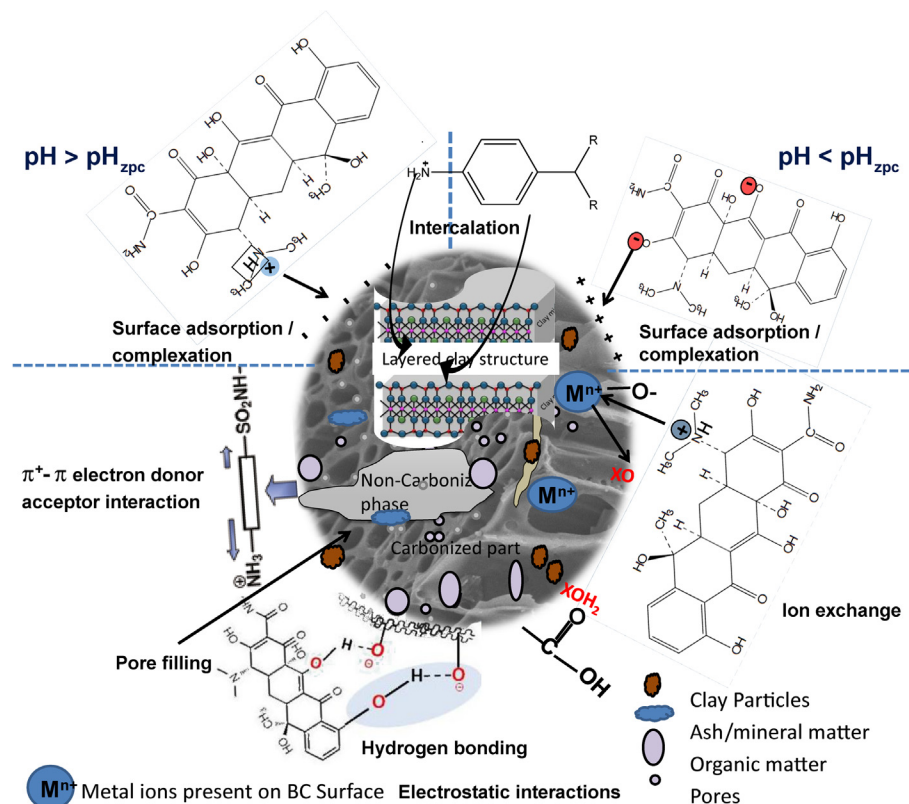


Figure 9.2 Adsorption mechanisms involved in adsorption of PPCPs onto biochar/engineered biochar. *PPCPs*, Pharmaceutical and personal care product.

9.6 Environmental factors influence for sorptive removal

The main environmental factors that influence the sorptive removal of PPCPs include solution pH, temperature, interfering substances, and ionic strengths of the contaminated area. Therefore the sorptive removal of PPCPs from environmental matrices can be variable not only between different types of PPCPs but also within the same PPCP molecule when presents in different environmental matrices.

Environmental pH has a key impact on the adsorption, because pH has direct influence on chemical nature of PPCPs. Since PPCPs have different pK_a values, they can predominantly exist in its cationic, anionic, or neutral form (Chang et al., 2014, 2016) depending on environmental pH. Therefore the sorptive removal process depends on nature of adsorbent and type of PPCPs. For example, at $pH < pH_{pzc}$ of the adsorbent, the surface is negatively charged which promotes adsorption of positively charged PPCPs via electrostatic interactions. At $pH > pH_{pzc}$

of the adsorbent, surface is positively charged and avoids adsorption of positively charged PPCPs due to electrostatic repulsion (Gao et al., 2012). Anionic species become the dominant form of some PPCPs with increasing pH. The electrostatic repulsion between the negatively charged adsorbent surface and anionic species of PPCPs would hence increase, resulting in decreased adsorption at higher pH (Han et al., 2013). Adsorption of norfloxacin depends on the pH of the medium, due to different ionizable groups available on norfloxacin (Li et al., 2017b). Adsorption of TC also decreased with the increase of pH in 4.0–8.0 range, because the dominant form of TC in higher pH is anionic form which repulsed by negatively charged biochar surface.

Sorption process can be exaggerated by the presence of interfering organic or inorganic compounds. Generally, in real environmental conditions, water/wastewater is with many cationic/anionic compounds, and they may interfere with the target compound removal process. Interfering substances may increase or decrease the sorptive removal process depending on target PPCP compound and the nature of sorbent. For instance, cadmium ions (Cd^{2+}) had positive effect for the sorptive removal of SMX by biochars (Han et al., 2013). Sorption of Cd^{2+} ions onto the biochar surface facilitates the neutralization of biochar surface, thereby reducing the electrostatic repulsion between the biochar surface and anionic SMX (Han et al., 2013). The existence of oxytetracycline significantly hinder the adsorption of carbaryl on the biochar produced at 600°C and 700°C, indicating a competing effect between oxytetracycline and carbaryl adsorption (Li et al., 2017a). Competitive sorption between different chemicals usually occurs at the solid–water interface and can influence on the adsorption characteristics and affinity of the adsorbent for each contaminant.

9.7 Conclusions and future perspectives

Until now, various sorbents including activated carbon, biochar, agricultural solid waste, industrial by-products, natural clay minerals, and biosorbents have been shown promising results to remove PPCPs in water and wastewater. The diverse chemical nature and change in specific properties of PPCPs with environmental factors make the sorption process more complex in the real environment. Hence research interest needs to be focused on highly efficient novel sorbents that are suitable for natural environment conditions. Also, to be noted, a single sorbent is usually ineffective for diverse groups of PPCPs due to their complex chemical nature. Therefore the combination of different physiochemical characteristics of sorbents could assist in removing PPCPs in real environmental contaminated water/wastewater. Moreover, specific properties of water/wastewater such as pH, ionic strength, other contaminants, temperature should be considered for the selection of proper sorbents. Advanced molecular-level spectroscopic investigations are recommended for better understanding of underlying sorption mechanisms.

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