Review

Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: A critical review

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GRAPHICAL ABSTRACT
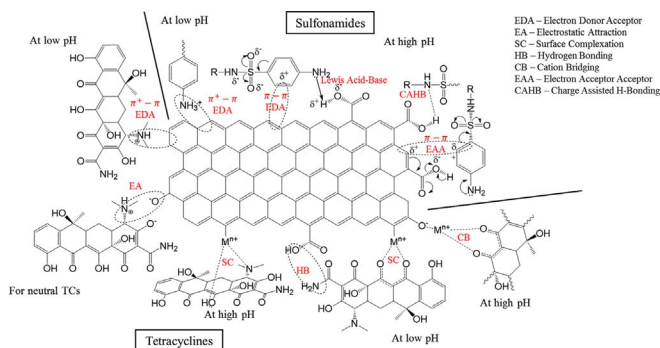
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ABSTRACT

Utilization of biochar (BC) as a low cost adsorbent for water remediation has gained an immense research interest due to their surface functionality and porosity. Although many reports on the BC based sorptive removal of Sulfonamides (SA) and Tetracyclines (TC) are available in literature, a deep insight into sorption mechanisms is yet to be reviewed. Objective of this review is to fill the research gap of a methodological understanding of sorption mechanisms and characteristics which is essential to develop efficient methods for contaminant removal. The most common adsorption mechanism can be considered as electron donor-acceptor interactions of electron withdrawing moieties with surface arene rings. The strongest adsorption of both antibiotics occurs at mildly acidic pH where the dominant species are zwitterionic or cationic. Smaller SAs exhibit micro pore-filling effects while bulky TCs experience size exclusions. Furthermore, the effect of matrix components and modifications are also been taken into account.

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1. Introduction

Pharmaceutically active compounds in aquatic environments are considered as an important class of contaminants of emerging concern (CEC) due to their extensive usage and resulting environmental pollution (Rossner et al., 2009). Hence, the removal of CEC which includes endocrine disruptors, pharmaceuticals, personal care products, plasticizers and flame retardants have gained significant attention due to their deleterious impact on human health and ecology (Covaci et al., 2011; Gunatilake et al., 2016; Yang et al., 2011).

Residual sulfonamides (SA) and tetracyclines (TC) are among the most frequently used antibiotics for therapeutic purposes and are also used as feed additives by certain intensive farming operations (Martucci et al., 2014; Yu et al., 2016). However, when used extensively, they pose potential hazards both environmentally and health wise (Shao et al., 2005). Antibiotics are not easily biodegradable and can cause numerous ecological impacts (Zhou et al., 2009). Residual antibiotics are capable of increasing the antibiotic resistance of bacteria in marine ecosystems resulting in the emergence of multi resistant bacterial strains which cannot be treated with drugs presently known. Bioaccumulation and biomagnification in aquatic organisms are another major ecological impact of residue antibiotics (Bai et al., 2014; Gao et al., 2012; Kim et al., 2014). Residual SAs and TCs can be carcinogenic on chronic exposure (Shao et al., 2005).

Biochar is an excellent biomass-derived carbonaceous sorbent for hydrophobic organic contaminants due to its surface aromaticity and functionality (Vithanage et al., 2016, 2014). Among many different sorbents, BC based sorptive removal has received enormous research focus in recent years due to its cost effectiveness and adsorption properties (Ahmad et al., 2014). It is possible for BC to be engineered for enhanced sorption (Ahmed et al., 2017; Mohan et al., 2014; Rajapaksha et al., 2016a). Several studies have reported the biochar based removal of different types of pharmaceuticals such as antibiotics, anti-inflammatory drugs (Jung et al., 2015; Vithanage et al., 2014) and other prescriptive and over the counter drugs (Karunanayake et al., 2017). Due to its increasing demand, pharmaceutical removal has even been introduced to undergraduate laboratory experiments (Karunanayake et al., 2016). Numerous studies and reviews on the sorptive removal of SAs and TCs can be found in literature. However, a research gap is created due to the fact that the attention given to the mechanistic understanding of the adsorption is minute. Therefore, the overarching objective of this review is to fill-up this gap by revisiting the literature focusing on mechanisms involved in the BC-Antibiotic interactions at the molecular level. This work provides a critical assessment of biochar based approaches for the removal of residual SAs and TCs via comprehensive evaluation of sorption mechanisms, dynamics and isotherm patterns.

2. Predictive analytics

A profound understanding of the science of antibiotic–BC adsorption can be extremely helpful for the optimization of sorption conditions. Three major aspects of such interaction are sorption affinity, capacity and dynamics. Sorption capacity depends on the available space of an adsorbent for adsorption of a given adsorbate. The strength of attractive and repulsive forces between the adsorbate and adsorbent determines the affinity of sorption. Sorption dynamics are determined by the initial concentrations, the contact time between the adsorbate and adsorbent as well as the diffusion properties of the adsorbate (Ahmed et al., 2015; Qiu et al., 2009).

2.1. Sorption kinetics

Adsorption phenomenon can be described in four consecutive steps; (1) solute transportation from the bulk, (2) diffusion across the liquid film surrounding the biochar particle, (3) diffusion in the liquid

contained in the pores and (4) interaction between adsorbate and adsorbent (Qiu et al., 2009). A number of adsorption kinetic models including pseudo-first order (PFO), pseudo-second order (PSO) and intra particle diffusion (IDM) have been developed to determine the adsorption mechanism and the potential rate-limiting steps. Non-linear data modeling is preferred with a comparison of Chi-square although numerous studies report linear data fitting with correlation coefficient (R^2) (El-Khaiary et al., 2010; Ho et al., 2005).

2.2. Sorption isotherms

The process of adsorption is usually studied through adsorption isotherms which are a characteristic feature for a specific adsorbent-adsorbate interaction at a given environmental condition. Such isotherms are extensively used to characterize the relationship between the adsorbed concentration and the dissolved concentration at equilibrium. Biochar-antibiotic interactions reported in the literature were mostly described using the two-parameter isotherm models, Langmuir and Fredluich. However, such sorption interactions are also described using the two-parameter Temkin and the three-parameter Redlich–Peterson isotherm models (Rajapaksha et al., 2015; Reguyal et al., 2017).

2.3. Sorption mechanisms

Sorption mechanisms of antibiotics on BC can depend on multiple factors including, (1) structural properties of the adsorbate, (2) physiochemical properties of the sorbent surface such as specific surface area, pore size distribution, surface functionality, ash content, etc. and (3) the conditions where the sorption is carried out such as pH and the nature of the matrix (interfering chemicals, humic substances present, etc.) (Chia et al., 2015; Inyang and Dickenson, 2015). Feedstock type and production methodology can be considered as the determining factors for surface morphology and functionality of a BC (Laird et al., 2009; Tan et al., 2015).

3. Sorptive removal of sulfonamides

3.1. Physiochemical properties of sulfonamides

Sulfonamides contain a 4-amino phenylsulfonylamide core structure. These sulfa drugs are classified into several groups depending on the substituent bound to the sulfonamide nitrogen. The most commonly used sulfanilamides which are discussed in this review include sulfamethoxazole (SMX), sulfamethazine (SMT), sulfapyridine (SPY), sulfathiazole (STZ), sulfanilamide (SNA) and sulfadiazine (SD).

3.2. Sorption mechanisms of sulfonamides

Salfonamides can act as strong π acceptors because the π systems of the two aromatic rings become electron deficient due to the strong electron withdrawing ability of the sulfonamide group. In SMX, the π electron density of the heteroaromatic group is further reduced due to high electro negativity of the O atom resulting in electronic resonance stabilization (Ji et al., 2009b). The amino functional groups also behave as π acceptors as they can donate the N lone electron pair to the aromatic rings (Ahmed et al., 2017). Salfonamides become stronger π acceptors at low pH as the protonation of amine groups and heteroaromatic N can further increase their π accepting ability (Acton, 2012; Wijnja et al., 2004). Thus, $\pi-\pi$ electron donor acceptor (EDA) interactions with π donating arene rings on the BC surface can be substantial and has been reported to be the most significant interaction between SAs on BC (Ahmed et al., 2017; Ji et al., 2011). At low pH where both SAs and char surfaces are positive, $\pi-\pi$ EDA interactions occurs between the protonated aniline ring and the π donating arene rings. This unusual $\pi-\pi$ EDA interaction and cation π bonding is referred to as

$\pi^+-\pi$ EDA interactions (Teixidó et al., 2011).

Hydroxyl groups directly bonded to aromatic rings can resonate as π donors increasing the π donor nature of the sorbent. In contrast, protonated carboxyl groups behave as strong π acceptors due to electronic resonance. Therefore carboxyl rich BCs become weaker adsorbents for SAs at low pH. Furthermore, low temperature produced BC (LTBC) can act as π acceptors due to their high content of surface carboxyl groups (at pH where carboxyl groups are protonated) whereas high temperature produced BC (HTBC) can act as π donors due to the high content of electron rich arene rings (Ahmed et al., 2017).

Further, it is mentioned that the $\pi-\pi$ electron acceptor-acceptor (EAA) interactions can also occur at positive SA sites with surface aromatic rings and protonated carboxyl groups(Ahmed et al., 2017). However, the EAA interactions may not be stabilized due to charge repulsions. It is important to note that protonated carboxyl and hydroxyl groups are capable of forming H-bonds with O and N atoms in neutral SAs (Ahmed et al., 2017). At sufficiently high pH (about two units higher than respective pKa values), stronger Lewis acid base interactions can occur between the basic groups of SAs and the aromatic carboxyl and hydroxyl groups of the carbonaceous surface (Ahmed et al., 2017).

When both the BC surface and the SA are negative, charge assisted hydrogen bonding (CAHB) interactions can occur which assist sorption. If the pK_a values of the BC surface functional groups (SFGs) and the SA are comparable (Ex: SMX $pK_{a_1} = 1.7$; $pK_{a_2} = 5.7$; i.e. with BC of pK_a around 4–6) and the pH is approximately 2 units higher (~ 8), the free energy associated with hydrophobicity is insufficient to overcome the proton exchange penalty (Ahmed et al., 2017; Mao et al., 2013; Teixidó et al., 2011).

High oxygen containing SFGs (O-SFGs) may facilitate the formation of dense hydrated layers on the BC surface restricting SA sorption. This effect can be significant at low solute concentrations (Mao et al., 2013; Zheng et al., 2013). Nonspecific Van der Waals forces are also a factor in sorption interactions (Ahmed et al., 2017). Adsorption can be facilitated by the presence of a metal ion such as Cu^{2+} through cation bridging (Morel et al., 2014). Also, micro pore filling or size exclusion interactions can occur in the presence of a low solute concentration and significant pore effect of the sorbent (Ji et al., 2011; Zheng et al., 2013).

3.2.1. Effect of pH in the sorption of sulfonamides
3.2.1.1. Effect of pH in SMX sorption.
Adsorption capacities and sorption distribution coefficients can vary significantly with change in pH as a result of simultaneous and numerous sorption mechanisms. Ahmed et al. observed a maxima of sorption capacity at pH = 3.25 for bamboo BC (ZP = 2.5) when the sorption was dominated by EDA interactions. Another maxima at pH = 6 was observed due to the interaction of negative and neutral species which resulted in a proton transfer from BC to SMX. Minimal capacity was observed at low pH (pH < 1.6) due to electrostatic repulsions as both SMX and BC surfaces are positive. Low capacities were also observed at pH = ~ 7 due to charge repulsions. A gradual increase in capacity was observed with increasing pH (up to 10) due to CAHB formation (Ahmed et al., 2017). This hypothesis was also supported by Zheng et al. where maximum sorption was reported when the pH of the medium was ~ 3–4 due to $\pi-\pi$ EDA interactions. However, a second maxima was not reported and the capacities decreased with increasing or decreasing pH due to charge repulsive forces (Zheng et al., 2013).

The adsorption properties of SMX on rice straw and alligator flag BC (reported pH_{PZC} was between 2 and 3.5) was compared (Li et al., 2015). Rice straw BC displayed maximum adsorption around pH 3 which gradually decreased with increasing pH due to stronger electrostatic repulsions. However alligator flag BC showed minimum adsorption at this pH, a gradual increase and a maximum at pH = 7, followed by a decrease of adsorption at higher pH. Majority of the O-SFGs were protonated at acidic pH making an electron accepting surface. As the pH increases, the anionic SMX percentage increases allowing stronger electrostatic interactions. However, above neutral pH, O-SFGs get deprotonated and reduced adsorption is observed due to electrostatic repulsions between negatively charged species (Li et al., 2015).

3.2.1.2. Effect of pH in SMT sorption.
The effect of pH on SMT sorption for bamboo BC (ZP = 2.5) was investigated by Ahmed et al. Sorption capacity was minimal at low pH (pH < 2) and gradually increased until reaching a maximum capacity at pH = 4.5. Capacities then gradually decreased until pH = 7, increased at pH = 8 and then again decreased at pH > 9. This variation is explained by the dissociation constants of SMT ($pK_{a_1} = 2.3$, $pK_{a_2} = 7.4$). When the pH was below 2, both solute and the BC surface were positively charged. The increment of sorption capacity is explained by the enhancement EDA interactions due to the zwitterion formation and the maximum adsorption pH = 4.5 is as a result of the stabilization of the zwitterion through strong H-bond formation and $\pi^+-\pi$ EDA interactions. At pH above 4.5, the sorption was restricted by the negatively charged SMT species and the sorbent surface. Intersections between neutral and negatively charges species were responsible for the second maxima. It is important to note that CAHB interactions facilitate sorption at elevated pH (Ahmed et al., 2017). Patterns reported by several other research groups are in agreement with this explanation. Teixido et al. removed SMT using hardwood litter BC prepared by slow pyrolysis at 600 °C (ZP = 4.1) and the maximum sorption is observed between pH ~ 3 and 6 due to zwitterion stabilization (Teixidó et al., 2011). He et al. also reported a study on the removal of SMT using carbonaceous α-cellulose. Maximum sorption capacities were observed at pH ~ 4–7 and significantly reduced capacities were observed at pH 3 and 8 (He et al., 2016). Sorption capacities were significantly decreased when the pH was further increased (~ 9) due to electrostatic repulsions of negatively charged species. Tea-waste and an invasive plant *Sicyos angulatus* L. was used as the feedstock in the reported studies (Rajapaksha et al., 2014, 2016b, 2015).

Though physiochemical properties and sorption mechanisms of all SAs are comparable, the dominant species at a given pH can be different due to differences in pK_a values. For example, SNA has a weak second dissociation ($pK_{a_2} = 10.6$) compared to that of other SAs. Thus at a pH of ~ 7–9, SNA mainly exists in the zwitterionic form while another SA with a stronger second dissociation (such as SMX or SMT) exists in its anionic form. Thus the effect of pH on sorption can slightly vary for different SAs. The pH dependence of such sorption also depends on the nature of the BC surface.

3.2.2. Effect of matrix components
3.2.2.1. Effect of co-existing metal ions in solution.
Sulfamethoxazole biochar interactions can be enhanced by the presence of Cd^{2+} (Han et al., 2013). A considerable enhancement of SMX sorption on rice straw BC (slow pyrolyzed at 400 °C) in the presence of Cd^{2+} ions was reported due to the effect of cadmium binding in the impregnated BC which reduced the surface negative charge, facilitating the sorption of neutral and anionic SMX (Han et al., 2013).

An inhibition of the sorption of SMX and SPY was reported on pine wood BC in the presence of Cu^{2+} ions (Xie et al., 2014). Adsorbed Cu^{2+} can have dense hydrated spheres hindering the available sites for hydrophobic interactions of solutes. Also, Cu^{2+} directly competes for sorption sites due to inner-sphere complexation (Xie et al., 2014). Co-existing Cu^{2+} could complex with anionic SAs and mitigate the negative charge facilitating sorption. Therefore, it can be concluded that the co-existing Cu^{2+} can enhance the sorption of surfaces that have less SFGs while inhibiting the sorption on functional group rich carbonaceous surfaces.

Insignificant changes were observed in SPY sorption capacity on nanotube modified BC in the presence of Pb^{2+} (Inyang et al., 2015). The observations were explained in terms of predominant site specific sorption mechanisms and insignificant competition for functional groups by the two co-existing sorbates. It was mentioned that the

modification gave rise to distributed and stabilized individual CNT nanoparticles on the biochar surface that were expected to adsorb more SPY compared with raw BC (Inyang et al., 2015).

3.2.2.2. Effect of humic acid in solution. Humic acids (HA) contain numerous polar moieties including carboxyl, phenolic, carbonyl, amino and methoxy groups (Lian et al., 2015). Humic Acids can strongly interact with the polar fraction of BC through H bonding and with hydrophobic fraction through $\pi-\pi$ EDA interactions (Lian et al., 2015). The authors have studied the sorption of SAs to HA coated BC. At neutral pH, coated BC showed enhanced sorption for anionic SMX through CAHB. In contrast, zwitterionic SNA experienced a depleted sorption through direct competition for predominant $\pi-\pi$ EDA interactions. Further, it was concluded that the effect of co-existing HA is significantly concentration dependent (Lian et al., 2015).

At a working pH of ~6, HA mitigated sorption due to the blocking of pores reducing access to sorption sites of pinewood BC pyrolyzed at 400 °C (Xie et al., 2014). Humic Acids showed increased inhibition due to the same effect as the π donor nature of BC increased through demineralization (Xie et al., 2014). At the same time, electrostatic repulsions between HA and SA inhibited the sorption of SAs (Liu et al., 2015).

In a comparative study of the retention of the two antibiotics in the presence of HA, a substantial inhibition was observed in SMX sorption while the inhibition of TC was insignificant. The decrease in sorption of SMX is mainly due to the direct competition for sorption sites. In contrast, bulky TC showed stronger affinity towards BC and mineral components in soil and HA induced only a slight size exclusion effect resulting a minor mitigation (Ji et al., 2011).

3.2.3. Effect of pyrolysis conditions

Numerous research studies have been carried out to evaluate the effect of BC pyrolysis temperature on SMX adsorption. The majority of the studies report that HTBC has higher adsorption capacities than LTBC. This agrees with the hypothesis of $\pi-\pi$ EDA interactions of HTBC vs charge repulsions of LTBC (Mao et al., 2013; Srinivasan and Sarmah, 2015; Sun et al., 2016; Tzeng et al., 2016; Xie et al., 2014; Zheng et al., 2013). In contrast, certain studies have reported an opposite pattern where the sorption capacity of LTBC was higher than that of HTBC. Though the exact mechanism of this phenomenon is uncertain, authors mentioned the significant role of SFGs in sorption patterns (Yao et al., 2012). Lian et al. also observed higher capacity for SMX sorption on Danshen residue (Chinese medicine) BC produced under low temperatures. Authors have shown the thermodynamic feasibility of sorption on LTBC because of significantly increased enthalpies and entropies in their study (Lian et al., 2014).

A higher adsorption capacity was reported for SMT in tea-waste HTBC than that of LTBCs due to reduced interactions with water molecules due to fewer surface O-functional groups and the less dense hydrated film facilitated diffusion (Rajapaksha et al., 2014). Interestingly, negligible contribution of surface O-functional groups on SMX adsorption was reported indicating contrasting observations among literature (Srinivasan and Sarmah, 2015; Xie et al., 2014).

One of the other important features in HTBC is the low volatile compound content. Escaping of trapped volatile chemicals can cause pore formation increasing pore volume and surface area. High temperature BC provides higher sorption capacities for SMT due to low volatile chemical content (Liu et al., 2015). A study reported the presence of both open and closed vesicles in tea-waste HTBC (700 °C) indicating the formation and release of volatile compounds (Rajapaksha et al., 2014). At neutral pH (pH$_{PZC}$ of BC = 2), anionic SMX showed greater sorption on LTBC due to CAHB interactions with abundant SFGs. In contrast, neutral SNA displayed higher sorption on HTBC as a result of dominant $\pi-\pi$ EDA interactions (Lian et al., 2015).

The availability of arene rings for EDA interactions can be a determining factor of sorption capacities. In a sorption study of SMX on corn-cob bio-char supporting TiO$_2$, authors observed much higher adsorption capacities of BC composite than commercial TiO$_2$ as a result of $\pi-\pi$ EDA interactions between SMX and carbon sites of BC. However, the capacities were less than that of raw BC due the availability of more carbon sites (Kim and Kan, 2016). Ji et al. reported a study on SMX removal by using mineralized and demineralized wheat and maize residue black carbon produced by aerobic carbonization. Adsorption capacities were higher in the demineralized sorbents due to high availability of surface arene rings and increased surface areas. Raman spectra of demineralized BC had similar characteristics to that of graphitize carbon even though the structural order was much lower than pure graphite (Ji et al., 2011). Demineralization of high temperature BC increased the availability of arene rings for $\pi-\pi$ EDA interactions. In contrast, the demineralization process of LTBC facilitated the emergence of O-SFGs which were hidden by inorganic compounds resulting in more π acceptor properties on the surface. Authors also discussed the effect of H bond formation in LTBC facilitating SMX and BC interaction. Further, the study concluded that there is no change in SFGs by acid modification (Zheng et al., 2013). Demineralization was carried out by washing with a mixture of acids (HCl and HF).

Jung et al. prepared NaOH modified BC in the presence (3%) and absence of oxygen using loblolly pine chips by torrefaction. BC produced under oxygenated conditions (OBC) contained more aromatic carbon than BC produced under oxygen-free conditions (NBC) which contained a higher amount of methoxyl, O-alkyl and carboxyl groups. Though arene rings contribute to effective SMX adsorption via EDA, NBC has shown comparatively higher adsorption capacity due to high pore volume and surface area (Jung et al., 2013).

3.2.4. Effect of ash content

Low ash BC showed higher sorption capacities than that of high ash BC. High ash BC contains high surface oxygen content due to metal oxides, which weaken the sorption capability for SMX (Shimabuku et al., 2016). Low comparative sorption capacities of biochar at neutral pH were reported (Calisto et al., 2015). The LTBC (400 °C) had less surface area available for adsorption than that of HTBC (600 °C) due to high ash and volatile content (Tzeng et al., 2016).

3.2.5. Effect of biochar modifications

3.2.5.1. Value added BC for SMX sorption. Citric and malic acid treated (straw derived) BC indicated a noteworthy increase ($> 5\times$) of SMX sorption capacity due to (1) elevated microporosity of the treated BC and (2) the removal of dissolved organics and metal cations by breaking the linkages with BC surface (Sun et al., 2016). Interestingly, the effect of dual treatment, peroxide oxidation followed by acid modification showed no significant enhancement of sorption observed which may be due to the creation of a substantial amount of effective O-containing SFGs and the subsequent prevention of diffusion into the inner micropores (Sun et al., 2016). The effect of citric acid (ternary organic acid) was stronger than that of malic acid (binary organic acid). It is important to note that these acids were less likely to form complexes with SMX due to their dominant anionic structures at the tested pH (~6) (Sun et al., 2016).

Magnetically modified pine sawdust BC was prepared via oxidative hydrolysis of FeCl$_2$ to investigate the sorption of SMX (Reguyal et al., 2017). A strong magnetization was observed through the formation of single-phase Fe$_3$O$_4$ nanoparticles on the surface. Sorption capacity of BC supported TiO$_2$ was significantly higher than TiO$_2$ powder due to EDA interactions with SMX (Kim and Kan, 2016).

3.2.5.2. Value added BC for SMT sorption. Two post modifications were tested using oxalic and sulfuric acids which were chosen due to (1) the high H$^+$ activity of sulfuric and (2) the high ligand activity of oxalic (Vithanage et al., 2015). A significant increase in surface area and pore volume was observed in the modified BC. It was also concluded that O-SFGs increased due to oxidation during treatment. Sulfuric modification

was more effective than the oxalic treatment but the increase in sorption capacity did not match the increase in surface area as the created micropores were not compatible with the size of SMT. Quicker equilibrium time is another advantage of the modification (Vithanage et al., 2015).

Steam activation enhanced SMT sorption by enhancing porosity and surface area by creating new pores and enlarging the size of existing pores as it acts as a secondary partial gasification which liberates additional syngas from the carbonaceous surface. The method is also capable of increasing the surface area by removing trapped volatiles (Rajapaksha et al., 2014, 2016b). Surface polarity and hydrophilicity increases as a result of an oxygen exchange from a water molecule resulting in the oxidation of the carbon surface forming surface hydrogen complexes (Rajapaksha et al., 2016b). Further, the steam activation process causes a significant improvement in sorption kinetics due to increased availability of accessible porous structures with comparatively larger pore diameters. In contrast, no significant difference was observed in burcucumber BC as the surface originally contained a substantial amount of mesopores (Rajapaksha et al., 2014, 2016b). The surface area enhancement of plant based BC was insignificant compared to woody BC due to relatively high ash content and the elevated ash production by steam activation (Rajapaksha et al., 2015).

3.3. Sorption isotherms for sulfonamide – biochar equilibrium

3.3.1. Isotherms of SMX

Many studies have stated that isotherms of SMX adsorption onto BC can be fitted into both Langmuir and Freundlich models (Ahmed et al., 2017; Calisto et al., 2015; Han et al., 2013; Kim and Kan, 2016; Sun et al., 2016). Numerous studies have reported Freundlich type adsorption for SMX on BC (Ji et al., 2011; Jung et al., 2013; Lian et al., 2015; Liu et al., 2015; Shimabuku et al., 2016; Xie et al., 2014). The SMX adsorption studies fitting into Langmuir isotherm models with sediment, rice straw and alligator flag BC were also reported (Li et al., 2015; Mao et al., 2013). Further, SMX adsorption studies fitting into Redlich-Peterson isotherm models were observed for magnetic pine sawdust BC (Reguyal et al., 2017). A linear isotherm pattern of SMX on raw giant reed stem was reported suggesting partition driven sorption (Zheng et al., 2013). All reported BC based sorptive studies have observed non-linear isotherms indicating adsorption driven surface interactions. Cooperative adsorption of SMX onto TiO_2 coated corn cob BC (Kim and Kan, 2016). All the other reported SMX interactions have indicated weak free energies of sorption.

3.3.2. Isotherms for SMT and other SAs

Several literature reports state that the SMT sorption on BC (cow manure, hardwood litter and steam activated tea waste) is best described by nonlinear Freundlich model with exponents of ($0 < n < 1$) indicating weak free energies of adsorption (Rajapaksha et al., 2014; Teixidó et al., 2011; Tzeng et al., 2016). In a study on BC (steam activated burcucumber) based SMT sorption, the surface equilibrium was well fitted into both Freundlich and Temkin models suggesting a favorable chemisorption process as well as electrostatic interactions (Rajapaksha et al., 2015). In a study of the sorptive removal of SMT by three different BC (slow pyrolyzed hardwood litter, hardwood chips and mixed hardwood and fast pyrolyzed hardwood sawdust), Freundlich as well as Langmuir isotherm models were well fitted (Teixidó et al., 2013). The single sorption of SMX and STZ were well fitted into both Langmuir and Freundlich models whereas SMT was best fitted into the Freundlich model. However, in competitive sorption, SMX, SMT and STZ were fitted into the Langmuir model (Ahmed et al., 2017).

When all reported literature is considered, with rare exceptions, SA-BC sorption was well fitted into Langmuir and Freundlich isotherms. The Freundlich exponents were less than 1 in the majority of reports suggesting weak free energies of sorption. Non-linear isotherms of all studies except one study (Zheng et al., 2013) suggested adsorption

driven surface interactions for SAs on BC. However, due to highly variable observations, it is rather difficult to comment on the relationship between the BC feedstock, pyrolysis method and sorption pattern. Hence, a systematic statistical study would be required.

3.4. Kinetics of sulfonamide sorption

Investigation of sorption kinetics of SAs and BC interaction using PFO, PSO, Elovich and IDM models have been reported in literature. The majority of the studies have observed PSO kinetic behavior indicating chemisorptive interactions for all considered SAs (Ahmed et al., 2017; Calisto et al., 2015; He et al., 2016; Jung et al., 2013; Rajapaksha et al., 2016b; Tzeng et al., 2016; Vithanage et al., 2015). In contrast, a PFO behavior of SMX sorption on coconut shell and bamboo BC was observed (Peng et al., 2016).

Single and competitive sorption of SMX and SMT on bamboo BC, reported a PSO behavior for single sorption and a diffusion controlled sorption in competitive media (Ahmed et al., 2017). A PSO type adsorption was observed at low solute concentrations while a PFO behavior was observed at higher concentrations on magnetized pine saw dust BC (Reguyal et al., 2017). Both PSO and PFO models failed to provide an idea of the exact sorption mechanism as the results fitted well in both cases. Further, the IDM also resulted in unsatisfactory correlation coefficients (Reguyal et al., 2017). A sorption study of SPY on carbon-nanotube modified BC which is best described by the Elovich model suggests strong chemisorptive interactions (Inyang et al., 2015). Identical correlation coefficients for both models were observed. However, the authors have concluded that the PFO model has the best fit by comparing the theoretically calculated equilibrium concentrations with experimental observations (Peng et al., 2016).

4. Tetracycline sorption in aqueous media

4.1. Physiochemical properties of Tetracyclines

Tetracyclines are a subclass of polyketides having an octahydrotetracene-2-carboxamide skeleton (Gold et al., 1997). The name "tetracycline" arises from the four hydrocarbon rings including a tricarbonyl (ring A) and a phenolic-β-diketone (rings BCD) system found in the chemical structure. Though TCs are classified into numerous groups depending on the substituents on the phenolic-β-diketone (BCD) rings, this review focuses on the removal of the three most common TCs; tetracycline (TC), chlorotetracycline (CTC), and oxytetracyline (OTC). Physiochemical properties of TCs and SAs are listed in Table 1.

4.2. Sorption mechanisms of Tetracyclines

The functional groups of TCs are capable of undergoing numerous electronic coupling interactions including π−π EDA, Lewis acid-base and electrostatic interactions. The conjugated enone structure influences the π acceptor properties of TC due to the strong electron withdrawing ability of the ketone group. Thus, specific π−π EDA interactions can be formed with π donating arene rings on the BC surface (Ji et al., 2009a). Phenol, amine, hydroxyl and enone moieties of TC can form H-bonding with carboxyl and hydroxyl functional groups on BC surfaces (Zhang et al., 2012). Cation π bonding interactions may also occur due to the easily protonated amine group at C4 (Ji et al., 2009a).

Cation exchange (CE) is a phenomenon where a positively charged organic molecule replaces naturally occurring cations associated with negatively charged sites on the sorbent surface. This is another favorable sorption mechanism for TC due to the cationic moiety at C4 (Ji et al., 2011; Lian et al., 2013). Cation exchange becomes a dominating factor for sorbents including iron/aluminum hydroxide, montmorillonite, etc. due to their exchangeable cation rich surfaces (Parolo et al., 2008). Hence significant CE interactions can occur on BC with high CEC, especially in acidic conditions where TC exhibits more

Table 1
Physiochemical properties of the interested antibiotics.

Name	CAS number	pk$_{a1}$	pk$_{a2}$	pk$_{a3}$	logk$_{ow}$	Solubility (g/L)	Molecular weight	References
Sulfonamides								
SMX	723-46-6	1.6	5.7		0.89	0.61	253.28	Ahmed et al. (2015), Yu et al.(2016), Ahmed et al. (2017)
SMT	57-68-1	2.65	7.65		0.14	1.5	278.34	Ahmed et al. (2015), Yu et al.(2016), Ahmed et al. (2017)
SPY	144-83-2	2.9	8.54		0.35	0.25	249.29	Ahmed et al. (2015), Yu et al.(2016)
SD	68-35-9	2	6.48		−0.34	0.067	250.28	Ahmed et al. (2015), Yu et al.(2016),
SNA	63-74-1	1.9	10.6		−1.36	7.35	172.2	Lian et al. (2015)
Tetracyclines								
TC	60-54-8	3.32	7.78	9.58	−1.37	22,000	444.43	Ahmed et al. (2015); Rivera-Utrilla et al. (2013)
OTC	2058-46-0	3.22	7.46	8.94	−0.9	17,000	496	Ahmed et al. (2015); Rivera-Utrilla et al. (2013)
CTC	64-72-2	3.33	7.55	9.33	−0.62	4200	515.34	Ahmed et al. (2015); Rivera-Utrilla et al. (2013)

cationic properties (Sassman and Lee, 2005).

Surface complexation (SC) is defined as a ligand exchange process where a hydroxyl group or a water molecule bound to surficial metal ion is displaced by a ligand group of an organic adsorbate (MacKay and Vasudevan, 2012). Though SC is not very common in biomass based chars, it can be a considerable phenomenon in certain synthetic feed-stock (Ex: tire waste, sludge) based chars (Lian et al., 2013; Rivera-Utrilla et al., 2013). Fig. 1 provides a graphical illustration of the mechanisms discussed.

4.2.1. Effect of pH in the sorption of Tetracyclines

A decrease in sorption at elevated pH (pH > ∼8) was observed on sludge based char and at pH values less than ∼8, higher sorption is expected due to $\pi-\pi$ EDA interactions occurring between zwitterionic TC and arene rings of the sorbent surface (Rivera-Utrilla et al., 2013). A decline in sorption at elevated pH is explained by the repulsive electrostatic interactions occurring between the negatively charged TC and the electron donating surface (Rivera-Utrilla et al., 2013). Similar decreased sorption of TC onto carbonaceous α-cellulose at elevated pH was reported in literature later (He et al., 2016). Though the sorption process was driven by non-specific van der Waals forces, authors mentioned the significance of H-bonding and EDA interactions at the tested pH.

A similar pattern for waste tire char (800℃,pH$_{PZC}$ = 7.8) was observed where the maximum sorption was at pH 7.1 (Lian et al., 2013). As the pH$_{PZC}$ suggests, the BC surface is positively charged at low pH making weak $\pi-\pi$ EDA interactions with cationic TC. Enhanced

sorption was observed with increasing pH as a result of strengthened EDA interactions with zwitterionic TC. Repulsive electrostatic interactions occurred at high pH (pH > 7.1) lowering the sorption process (Lian et al., 2013).

The pH dependence of OTC sorption on maize-straw BC has also been reported. The pH of the medium ranged from 2 to 10 and the maximum adsorption was obtained at pH = 5.5. A slight increase in pH was observed at pH 3.5 and 5.5 indicating the sorption of OTC with the uptake of protons. It was concluded that the OTC was adsorbed either through SC or CE in the form ofOTC⁰−H⁺(Jia et al., 2013).

4.2.2. Effect of the metal ions in solution

Literature examples report both enhanced and reduced sorption of TC when the ionic strength of the solution is increased. A few studies have been carried out to compare adsorption capacities in the presence and absence of NaCl (He et al., 2016; Rivera-Utrilla et al., 2013; Tan et al., 2016). Though hydrophobic partition is less favorable in TCs due to high hydrophilicity, the sorption capacities can increase with increasing ionic concentration of the solution due to the salting out effect which makes TC less soluble (He et al., 2016). In contrast, ions in solution could cause an electrostatic screening effect which reduces adsorption capacities. When the carbon surface is charged at neutral pH, attractive electrostatic interactions can occur with partially ionized TC molecules. The presence of Na⁺ and Cl⁻ ions can reduce attractive electrostatic interactions due to an electrostatic screening effect as they can be placed between the carbon surface and partially ionized TC molecules (Rivera-Utrilla et al., 2013; Tan et al., 2016). In addition, Na⁺
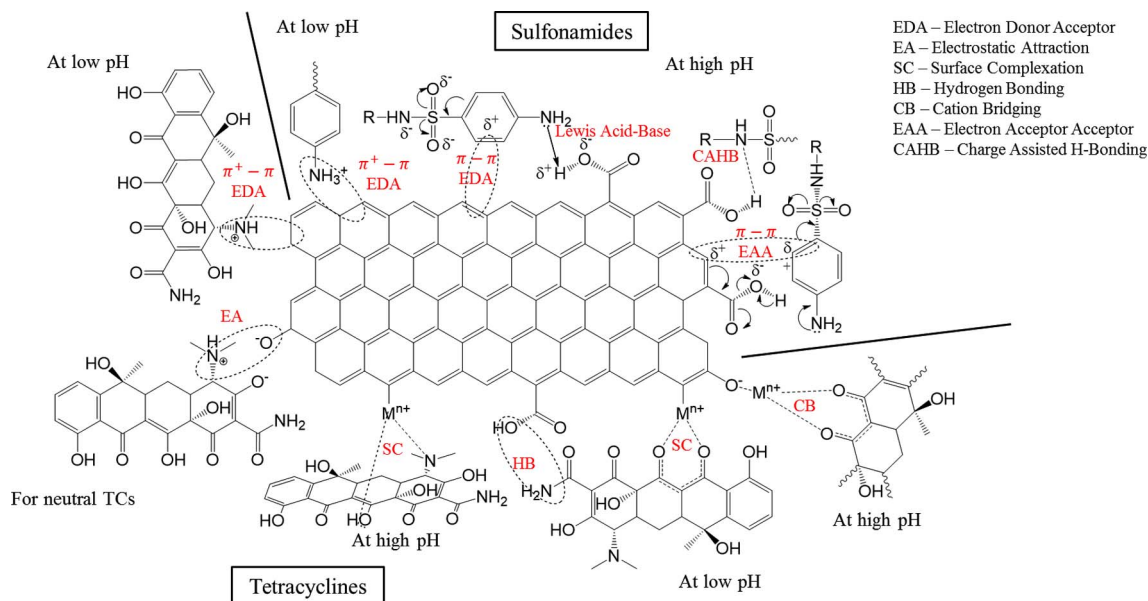

Fig. 1. Graphical illustration of adsorption mechanisms during the adsorption of sulfonamides and tetracyclines on biochar surfaces.

is capable of occupying active sites which are available for TC adsorption (Tan et al., 2016).

At pH levels of ~3.5–7.5, TCs exist predominantly in zwitterionic form and tend to aggregate in aqueous solution (Sassman and Lee, 2005). The aggregation is enhanced in the presence of divalent metal ions increasing the solubility of TC due to cosolvent solubilization (Tongaree et al., 1999). Tetracyclines strongly chelate with monovalent and multivalent cations in alkaline pH due to negatively charged hydroxyl groups and the electron donating ability of deprotonated nitrogen at C4 (Kulshrestha et al., 2004; Sassman and Lee, 2005).

The effect of metal ions including K^+, Ca^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} on TC adsorption was studied indicating that the SC was the most favorable sorption mechanism because the BC surface as well as the OTC sorbate were negatively charged at the tested pH (5.5) (Jia et al., 2013). Cu^{2+}, Pb^{2+} and Zn^{2+} form inner sphere complexes with hydroxyl and carboxyl groups on the BC surface while Cd^{2+} forms outer sphere complexes. The presence of Cu^{2+} enhanced sorption due to the formation of stable complexes with the β-diketones of OTC. Complex formation of OTC with Zn^{2+} is not as stable as that of Cu^{2+} resulting in insignificant enhancements in adsorption. In contrast, Pb^{2+} slightly decreased sorption capacities as it blocks the available sorption sites and is also incapable of forming stable complexes with OTC due to relatively low formation constants. The effect of Cd^{2+} was also negligible as the sorption of Cd^{2+} and BC was not governed by SC (Jia et al., 2013). The mutually facilitated sorption of TC and Cu^{2+} due to SC and cation bridging has been reported in the literature (Lian et al., 2013).

4.2.3. Effect of pyrolysis conditions

Zhang et al. (2012) compared sorption characteristics of TC on corn straw BC produced at different temperatures (100–600 °C). H-bonding with polar SFGs were significant in LTBC whereas $\pi-\pi$ EDA interactions with arene rings were prominent in HTBC. The highest sorption affinity was observed in the 600 °C BC due to increased surface area and pore volume by pore expansion and graphene sheet rearrangement (Zhang et al., 2012). A similar study carried out by the same research group using corn straw BC produced from 400 to 600 °C also produced comparable results. However, it was reported that clay minerals are much more efficient sorbents of TC in comparison with BC due to strong interactions such as CE and SC (Zhang et al., 2013). Zhu et al. also reported the decreased sorption of TC onto LTBC (by hydrothermal conversion (HTC) of *Salix psammophila*) reasoning that the inhibition is caused by dense water clusters around polar functional groups (Zhu et al., 2014 b). In agreement with the above observations, Fu et al. (2016) reported enhancement of sorption of OTC by (350–650 °C) pineapple peel BC when pyrolyzed under higher temperatures.

Pyrolysis temperature is a significant factor governing pore distribution. Zhu et al. produced HTC-BC from *S. psammophila* at 300–700 °C and reported higher surface area in HTBCs which facilitated TC sorption (Zhu et al., 2014b). Surface area and total pore volume increased with increasing pyrolysis temperature in the waste tire char as it facilitated the polymer breakdowns and removal of small molecules. However, when the temperature was increased beyond 800 °C, surface area and pore volume were slightly decreased as the micropores became mesopores and macropores due to the destruction of pore walls between adjacent pores (Lian et al., 2013). Improved sorption of sludge based char pyrolyzed at 750 °C was demonstrated as the mesoporous surface facilitated the diffusion of TC into pores (Yang et al., 2016).

4.2.4. Relative sorption properties of Tetracyclines

Electron density of the aromatic ring as well as the bulkiness decreases in the order of TC > OTC > CTC. Electron density is a key factor governing the strength of EDA, H-bonding and electrostatic interactions favoring sorption. In contrast, larger TC species experience stronger size exclusion effects, decreasing sorption capacities (Rivera-Utrilla et al., 2013).

4.2.5. Modified biochar in tetracycline sorption

The effect of methanol modification in fast pyrolyzed (rice husk) BC for TC removal can be found in literature (Jung et al., 2013). Post modified BC showed enhanced sorption as well as improved equilibrium time. Modified BC led to enhancement in sorption capacity as well as improvement of equilibrium time. Authors observed a reaction between methanol and carbonyl groups to produce ester groups. The decrease of electron withdrawing carbonyl groups and the consequent increase of electron donating ester groups facilitated $\pi-\pi$ EDA interactions with TC. Further, the methanol treatment reduced inherent organic compounds increasing the effective surface area for adsorption. The equilibrium times of modified char were improved as the mesopore dominating structure assisted pore diffusing (Jing et al., 2014). The effect of acid modified and alkali modified (fast pyrolyzed rice husk) BC on TC sorption demonstrated a better sorption at alkali modification due to increased surface area and decreased ash content facilitating $\pi-\pi$ EDA interactions with surficial arene rings (Liu et al., 2012). Alkali treated pinewood BC (fast pyrolysis at 525 °C) for the removal of CTC indicated an improved porosity by converting the smooth surface into pores (Taheran et al., 2016). Further, the oxygen content was reduced in the treated BC making the surface more hydrophobic resulting in considerably higher sorption capacities (Taheran et al., 2016).

Biochar production using iron loaded feedstock has become an emerging research interest (Peng et al., 2014; Yang et al., 2016). The effect of the iron loading on adsorption capacity was due to increased surface area, enhancement of H bonding and bridging effects (TC-Fe-BC) (Peng et al., 2014). Iron acted as a separation agent during HTC resulting in the shredding of the surface. The loading caused aggregation of carbon sheets to produce globular particle shaped morphology with increased surface area. FTIR results showed a significant decrease of surface −OH vibrations upon adsorption providing strong evidence of H-bonding. Iron oxides can deprotonate TC to form chemisorptive interactions through SC even at low pH (Peng et al., 2014). High adsorption capacities in BC produced from ferric loaded sludge was observed (Yang et al., 2016). Higher ferric concentrations destructed the microporosity due to hyper activation, and the resulting mesoporous carbon enhanced the sorption of bulky TC (Yang et al., 2016). In addition to the above factors, the effect of cation–π bonding on enhanced sorption of TC onto magnetically modified HTC-BC was also reported (Zhu et al., 2014a).

The Mg/Al layered double hydroxides on BC allowed enhanced $\pi-\pi$ EDA interactions and H-bonding. Authors also reported the significance of anion exchange interactions between anionic TC and the interlayer anion of the layered double hydroxides (Tan et al., 2016).

4.2.6. Comparative sorption studies involving Tetracyclines

Sulfamethoxazoles are compatible with micropore filling sorption due to their small size which results in higher sorption capacities than TC (Ji et al., 2011). A competitive sorption study of TC and metsulfuron-methyl (ME) on corn straw BC produced at 100–600 °C indicated greater hydrophobicity of ME and the compatible size for micropore filling, TC showed better sorption than ME at pH 5.5 due to the absence of electrostatic repulsions. Nonlinear Freundlich isotherms suggested adsorption dominated interactions of TC. An insignificant competition from ME sorption on BC produced at 100–300 °C was observed suggesting the partition of ME on rubbery domains (Zhang et al., 2012). The same BC was used to evaluate competitive sorption of TC, ME and simazine (SZ). Results were comparable for TC and ME. However SZ showed maximum sorption as a result of its small size and the hydrophobic nature (Zhang et al., 2013).

Though the mineral components are capable of enhancing the sorption of polar organic compounds through site specific EDA interactions, they can also decrease surface area and pore volume due to blocking of the access to non-specific sorption sites. The effect of demineralization of cow manure BC on the competitive sorption of OTC and carbaryl indicated that a weakened demineralization resulted in a

weak competitive sorption strength of OTC to carbaryl while enhancing that of carbaryl to OTC (Li et al., 2017). The dominant sorption mechanisms of OTC and carbaryl were pore filling and site specific interactions. Demineralization caused smaller carbaryl molecules to compete for the micropores eliminating bulky OTCs by size exclusion (Li et al., 2017).

Sulfamethoxazole sorption was governed by micropore filling while TC experienced a molecular sieving effect due to its large size (Ji et al., 2011). Despite the bulky nature, He et al. observed a higher sorption capacity for TC in a competitive study with SMT on carbonaceous α-cellulose. At the tested pH of 6, the zwitterionic TC contained abundant moieties capable of forming H-bonds while the carbon surface was rich in oxygen and nitrogen containing functional groups facilitating sorption (He et al., 2016).

4.3. Sorption isotherms for biochar – tetracycline interaction

Many sorption studies have carried out curve fitting of both Langmuir and Freundlich isotherm models. In several studies of TC sorption the Langmuir model was best fitted (Fu et al., 2016; Peng et al., 2014; Rivera-Utrilla et al., 2013; Taheran et al., 2016). An increase of sorption capacity with temperature indicating endothermic TC adsorption on carbonaceous α-cellulose was observed (He et al., 2016). In some studies, the Freundlich model was best fitted (Yang et al., 2016; Zhu et al., 2014a). However, some studies reported TC sorption fit well into both models (Liu et al., 2012; Tan et al., 2016). Once, a corporative adsorption was reported with Freundlich exponent greater than one for sludge based BC. In all other studies on TC sorption, Freundlich exponents were less than 1 signifying adsorption driven equlibrium with weak free energies (Ji et al., 2011; Jia et al., 2013; Li et al., 2017; Lian et al., 2013; Zhang et al., 2012; Zhang et al., 2013; Zhu et al., 2014b).

4.4. Kinetics of Tetracycline sorption

Similar to SMX, the majority of TC sorption studies were also best described by the PSO model indicating chemisorptive interactions for both raw and modified BC (Fu et al., 2016; Jia et al., 2013; Jing et al., 2014; Liu et al., 2012; Peng et al., 2014; Tan et al., 2016; Yang et al., 2016; Zhu et al., 2014a). However, Utrilla et al. and Peng et al. observed PFO type TC sorption (on sludge, bamboo and coconut shell BC) indicating dominant physisorption (Peng et al., 2016; Rivera-Utrilla et al., 2013). An enhancement of rate constants with the amount of surface carboxylic groups has been observed in a study (Ocampo-Pérez et al., 2012). Furthermore, a decrease in the PSO rate constant at higher concentrations of TC had been observed due to increased competition towards sorption sites (He et al., 2016).

Several studies have used the IDM to investigate the rate determining step of TC sorption. Multilinear IDM plots did not pass through the origin suggesting rate determining steps other than inter particle diffusion (Fu et al., 2016; He et al., 2016; Jing et al., 2014; Tan et al., 2016; Yang et al., 2016; Zhu et al., 2014a).

5. Critical assessment of mechanisms and Future directions

Numerous sorption mechanisms such as cation π bonding, π−π EDA interactions, H-bonding, electrostatic repulsions, CAHB, SC and cation bridging can be responsible for the sorption of SA and TC on BC. Significance of these mechanisms depends on properties of BC surface as well as conditions of solution. Sulfonamides can be either cationic, zwitterionic or anionic at different pH values depending on their pK_a values. Though sorption mechanisms of all SAs are comparable, the dominant species at a given pH can be different due to differences in the dissociation constants. Neutral SMX show strong π acceptor properties due to electron deficient aromatic rings. Thus, the strongest adsorption of SAs occur when the solute is neutral (pH ~ 3–4) due to π−π EDA interactions with π donating arene rings on BC surface. The highest

reported sorption of SMT also occurs at pH ~ 3–5 as a result of the stabilization of zwitterion through strong H-bond formation and $\pi^+-\pi$ EDA interactions.

In general, HTBCs are more suitable for SA sorption because (1) the surface is abundant with arene rings facilitating π−π EDA interactions, (2) thinner hydrated films which result in fewer of SFGs facilitating film diffusion (3), relatively low volatile content, and (4) higher pore volume and surface area. In contrast to majority of literature, a few studies report higher sorption of SAs into LTBC. Though the exact mechanism for this observation is uncertain, this implies the significance of SFGs on sorption. Negative CAHB can be considered the most significant interaction of SAs with O-SFGs at elevated pH.

Biochar with high ash content exhibit weaker sorption of SAs due to higher surface oxygen content. Demineralization of BC can affect the sorption of SAs positively as well as negatively. The process can enhance the sorption on HTBC by increasing the available arene rings. It can also decrease the sorption of LTBC by emerging O-SFGs hindered by inorganics which increases π acceptor properties of the surface.

Enhanced sorption of BC can be achieved by value addition. Various acid treatments of BC using inorganic acids as well as low molecular weight organic acids have been reported. Acid treatment can result in increased surface area and pore volume by the removal of inorganic minerals and dissolved organics. However, it can also increase O-SFGs. Certain acid treatments can cause surface oxidation. Steam activation can create new pores while enlarging the existing. Purpose of the modifications of BC sorbents can go beyond adsorption enhancement, for example, the magnetically modified BC reduces the recovery cost while TiO_2 coated BC enables the catalytic degradation of adsorbent.

Tetracyclines exhibit relatively high hydrophobicity in comparison with SAs. They act as triprotic acids and the amphoteric behavior is caused by the neutral and differently charged species dominating at different pH values. In addition to above mentioned electronic coupling interactions, cation bridging and SC play a significant role in TC sorption. According to majority of literature, zwitterionic TCs (pH ~ 4–7) show high adsorption due to π−π EDA interactions and H-bonding. Certain studies reported a reduction on solution pH upon adsorption indicating CE and SC as driving force for sorption.

It was reported that TCs can strongly chelate with mono and divalent cations at alkaline pH. Also, the solubility of zwitterionic TCs are enhanced in the presence of divalent metal ions through cosolvent solubilization. Dominant SCs are observed with coexisting metal ions at pH values where the both TC and BC surface is negatively charged. Enhanced sorption can be achieved with Cu^{2+} due to inner sphere complex formation. However, the same enhancement is not observed by (1) Zn^{2+} due to the relative instability of complexes (2) Pb^{2+} due to its ability to block sorption sites and (3) Cd^{2+} due to outer sphere complex formation. Considering all published literature, it can be concluded that HTBC is more suitable for TC removal. Pore size of the adsorbent is a critical factor for efficient adsorption. Carbonaceous surface of BC mainly consists of micropores. Thus, smaller SA molecules are more likely to undergo micropore filling while bulky TCs experience size exclusion effects.

Majority of the reported studies obey PSO kinetic patterns suggesting dominant chemisorption. Further, literature suggests that the rate determining step of such sorption is either film or bulk diffusion. Sorptive removal of these antibiotics commonly follows Langmuir and Freundlich isotherm patterns and the nonlinear isotherms indicate adsorption dominated interactions on glassy domains of BC.

Sorption of TCs using biochar mineral composites needs more attention due to their high CEC. Efficient regeneration methods of BC should be discovered and also further consideration should be driven into photocatalytic and biodegradation of adsorbate on sorbent surface. Competitive sorption of SAs and TCs require extra attention as the remediations are done mostly in natural aqueous ecosystems. Models which allow the exact determination of the rate determining step will be helpful for method optimization. Thus, actions can also be taken

place to reduce equilibrium times by shifting rate determining steps.

Though surface functionalities and physiochemical properties of BC largely depend on the feedstock type, information available on the effect of feedstock on antibiotic removal is rather limited. Hence, more comparative studies should be carried out to identify best biomass types to be used in BC based antibiotic removal.

6. Conclusions

The mechanisms responsible for the adsorption of SAs and TCs have been comprehensively reviewed. Generally, HTBC shows high adsorption at mildly acidic conditions due to strong EDA interactions between abundant π donating arene rings on BC surface and π accepting protonated adsorbates. Further, mechanisms such as electrostatic interactions, CAHB, SC, CE, and nonspecific Van der Waals interactions can also occur during adsorption. Micropore filling is common in SAs due to their smaller size. Thorough understanding of mechanisms are essential for efficient adsorptions as surface interactions depend on various factors such as pH, SFGs, pore characteristics and co-existing matrix components.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.07.150.

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