Biochar based sorptive remediation of steroidal estrogen contaminated aqueous systems: A critical review

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ABSTRACT

Remediation of steroidal estrogens from aqueous ecosystems is of prevailing concern due to their potential impact on organisms even at trace concentrations. Biochar (BC) is capable of estrogen removal due to its rich porosity and surface functionality. The presented review emphasizes on the adsorption mechanisms, isotherms, kinetics, ionic strength and the effect of matrix components associated with the removal of steroidal estrogens. The dominant sorption mechanisms reported for estrogen were π–π electron donor-acceptor interactions and hydrogen bonding. Natural organic matter and ionic species were seen to influence the hydrophobicity of the estrogen in multiple ways. Zinc activation and magnetization of the BC increased the surface area and surface functionalities leading to high adsorption capacities. The contribution by persistent free radicals and the arene network of BC have promoted the catalytic degradation of adsorbates via electron transfer mechanisms. The presence of surface functional groups and the redox activity of BC facilitates the bacterial degradation of estrogens. The sorptive removal of estrogens from aqueous systems has been minimally reviewed as a part of a collective evaluation of micropollutants. However, to the best of our knowledge, a critique focusing specifically and comprehensively on BC-based removal of steroidal estrogens does not exist. The presented review is a critical assessment of the existing literature on BC based steroidal estrogen adsorption and attempts to converge the scattered knowledge regarding its mechanistic interpretations. Sorption studies using natural water matrices containing residue level concentrations, and dynamic sorption experiments can be identified as future research directions.

1. Introduction

Endocrine disrupting chemicals (EDC) of both natural and anthropogenic origin are known to interfere with the endocrine systems of both humans and animals by mimicking the activity of endogenous hormones, thereby changing normal physiological functioning (Li et al., 2010; Lv et al., 2016). Endocrine disrupting compounds are a rapidly emerging area of concern because these compounds can elicit deleterious health effects in animals and their progeny who are exposed. Endocrine disrupting chemicals, which include, but are not limited to synthetic steroids, gonadal steroids, phytoestrogens and industrial chemicals, evoke their effects on animals by binding with nuclear receptors, non-nuclear steroid hormone receptors, non-steroid receptor

and orphan receptors. Furthermore, they can impact biochemical pathways of steroid synthesis and metabolism (Diamanti-Kandarakis et al., 2009; Gunatilake et al., 2013; Wathudura et al., 2019).

Steroidal estrogens are considered to be the most potent type of EDC due to their high affinity towards estrogen receptors, a type of nuclear receptor (Gomes et al., 2004; Gunatilake et al., 2016; Hanselman et al., 2006). Examples for these include natural estrogens, such as estrone (E1), 17β-estradiol (βE2), 17α-estradiol (αE2), and estriol (E3) and the synthetic estrogen ethinyl estradiol (EE2). Estrogen based medicines and synthetic sex steroids are used frequently by humans and the livestock industry respectively (Hulley et al., 1998; Mulnard et al., 2000). Therefore, significant quantities of hormones are released in the form of excreta such as urine and feces (Huang and Sedlak, 2001; Zuehlke et al.,

2005).

Areas with high population densities are potent sources of environmental estrogens because the release of estrogens into municipal waterways lead to estrogen accumulation in wastewaters, especially in highly urbanized areas (Gunatilake et al., 2014a). Wastewater treatment plants are a potential pathway for estrogens to enter the environment, as any estrogen not removed during the treatment process are released into the waterways (Gunatilake et al., 2014a). When lagoon wastewater is used to meet crop nutrient requirements, fields become contaminated with estrogens. During storms and snowmelt events, surface runoffs can result in the release of estrogens into surrounding aquatic bodies (Gunatilake et al., 2014b).

Estrogens are known to cause detrimental changes to aquatic life forms when present even at very low concentrations (Gunatilake et al., 2014a; Jobling et al., 1998; Purdom et al., 1994). For example, when 17β estradiol (βE2) is present at ppt levels in aquatic systems, vitellogenin production is induced in male rainbow trout in a dose-dependent manner (Jobling et al., 2003; Streck, 2009). Generally, vitellogenin is expressed in females as an egg yolk precursor protein. Other notable side effects include reproduction dysfunctionality and DNA damage in aquatic wildlife (Colborn et al., 1993; Toppari et al., 1996). Similarly, estrogenic endocrine disruptors are capable of causing obesity, testicular cancer and infertility in humans (Bouskine et al., 2008; Diamanti-Kandarakis et al., 2009; Newbold et al., 2009).

Several methods exist to purify water bodies containing estrogens, which can be divided into two main groups; adsorptive and non-adsorptive (Racz and Goel, 2010). Non-adsorptive methods such as oxidative processes and biological treatment have limited applicability due to their high energy demand and production of toxic by-products (Pereira et al., 2011). Examples of adsorptive methods recorded in literature include the usage of multi-walled carbon nanotubes to remove E2, industrial-grade polyamide 612 to remove EE2 and nanoscale zero-valent iron particles to remove E2 and EE2 from water (Han et al., 2013; Jarošová et al., 2015; Jiang et al., 2017).

Biochar (BC) is a porous, carbonaceous adsorbent derived from the carbonization of lignocellulose rich biomass. It is widely used to remediate pharmaceuticals, pesticides, organic contaminants and industrial dyes from aqueous systems (Ahmad et al., 2014; Inthapanya et al., 2019; Zhu et al., 2018). The sorptive removal of inorganic compounds such as heavy metals, halides and oxyanions are other applications of BC (Jayawardhana et al., 2019; Karunanayake, 2019; Navarathna et al., 2019, 2020; Rajapaksha et al., 2013). Over the years, BC has received attention as a soil amendment as well due to its ability to act as a nutrient source, to retain nutrients and for the removal of toxic contaminants (Peiris et al., 2019a; Wu et al., 2017).

Organic waste is often employed as feedstock for the production of BC as it is abundantly available and assists in waste management (Jayawardhana et al., 2019; Usman et al., 2015). Among many different sorbents, BC based sorptive removal has received enormous research interest in recent years due to its economic feasibility and adsorption properties. The physicochemical properties of BC are influenced by the feedstock type and pyrolysis conditions (Peiris et al., 2019b). Value additions of BC can be performed either via pre or post pyrolysis, which enhances the physicochemical properties of a given adsorbate, thereby leading to enhanced adsorption properties (Mayakaduwa et al., 2017; Peiris et al., 2019b; Rajapaksha et al., 2016).

Composite materials have gained attention recently due to the enhanced sorption properties that result due to the combined effect of multiple raw materials. Several such composites include graphene based composites, carbon nanotube based composites, CuO–ZnO composite nanofibers etc. (Kim et al., 2018; Malwal and Gopinath, 2017; Yu et al., 2014). In contrast to BC-based composites, many of the other composite types (1) require special technical expertise for production, (2) can be relatively expensive, and (3) might not contribute to solid waste management.

Recent work on the remediation of steroidal estrogens using BC and BC-composites show promise, and numerous studies on the sorptive removal of estrogens using BC produced from various feedstocks under different pyrolysis and sorption conditionshave been reported. Remediation of estrogens from aqueous solutions have been discussed in reviews that cover a collective evaluation of micropollutants (Mohan et al., 2014; Tong et al., 2019b). However, to the best of our knowledge, this is the first critique focusing specifically and comprehensively on BC based removal of steroidal estrogens. This review aims to address the research gap created due to the widely scattered knowledge and provides a comprehensive one-stop pool of information required for a proper mechanistic understanding of the sorption of estrogens. Therefore, the goal of the presented work is to revisit relevant literature, and provide mechanistic interpretations and dynamics associated with BC based sorptive removal of estrogen. This review caters to a comprehensive understanding of the sorption behavior involved in the BC-based removal of steroidal estrogens.

2. Physicochemical properties and structural basis of steroidal estrogens

Steroidal estrogens are derivatives of cholesterol, commonly comprising a cyclopentan-o-perhydrophenanthrene skeleton (Fig. 1a and b), where only ring 'A' exhibits aromatic properties. Estrogens are classified into several groups depending on the substituents at C-16 and C-17 of the five-membered ring (Hanselman et al., 2003; Khanal et al., 2006). This review focuses on the remediation of three major naturally occurring estrogens, estrone (E1), estradiol (E2), and estriol (E3) and the synthetic pharmaceutical ethinylestradiol (EE2). The molecular weights of estrogens range from 270.37 to 296.40 g mol^{-1} and the molecular volumes range from 3.81×10^{-22}- 4.06×10^{-22} cm^3. They exist as undissociated compounds in aquatic ecosystems owing to their high pKa values (10.2–10.8) (Ahmed et al., 2018; Wathudura et al., 2019). Estrogens have vapor pressures ranging from 10^{-10} to 10^{-15} mm Hg and they also have high octanol-water partition coefficients (K_{OW} = 2.81–4.20) (Ahmed et al., 2018). Therefore, it can be concluded that estrogens are non-volatile and moderately hydrophobic organic compounds with low aqueous solubility. The physicochemical properties of the estrogens discussed are shown in Table 1.

3. Sorptive removal of steroidal estrogens

3.1. Mechanisms of biochar-estrogen interactions

The phenolic group of estrogen is capable of donating electrons to the benzene ring to make a resonance stabilized structure. The enhanced electron density of the benzene ring allows it to act as an effective electron donor (Fig. 1d and e) (Ahmed et al., 2018; Dong et al., 2018; Yin et al., 2018). The electron donor properties can vary slightly from one estrogen to another depending on the different substituents attached to the five-membered ring. The pKa values of the four estrogens considered range from 10.2 to 10.8 (Table 1) Kim et al., 2009; Lai et al., 2000; Tabak, 1981. When the pH of the medium is equal to the pKa of estrogen, the ionized and neutral forms of the estrogen will exist in equal concentrations. As the pH increases above the pKa, the concentration of the ionized species in the medium increases and becomes predominant. Two pH units below the pKa, the estrogen will exist almost exclusively in its neutral form (Fig. 1c). As reported by Ahmed et al., at extremely acidic pH (pH ≤ 2), the hydroxyl and ketonic groups will be protonated and the estrogen will exist in its cationic form (Ahmed et al., 2018).

Biochar can act as either an electron acceptor or donor depending on the extent of functionalization and graphitization of the BC surface (Peiris et al., 2017). A BC that is produced at low temperature is usually rich in oxygenated surface functional groups (O-SFGs) such as hydroxyl, carbonyl and carboxyl (Dong et al., 2018; Peiris et al., 2017). Over a wide range of pH (pH 3–12), the hydroxyl groups attached to the arene rings on the BC surface can function as electron donors, whereas the
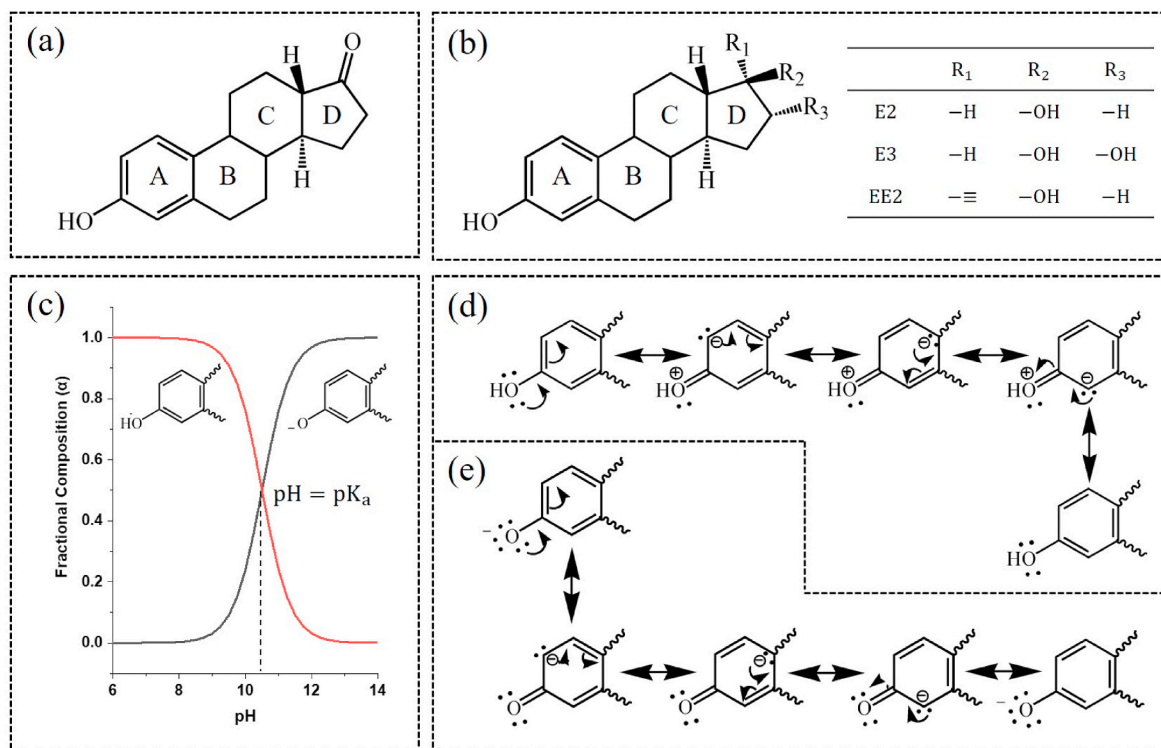
Fig. 1. (a) Structure of E1, (b) Structure of E2, E3 and EE2, (c) Speciation diagram of E2, (d) Resonance stabilization of protonated estrogens, and (e) Resonance stabilization of deprotonated estrogens.

Table 1
Physicochemical properties of several steroidal estrogens of interest.

Estrogen	Chemical Formula	CAS	Molecular weight (g/mol)	γ_{sat} (mg/L at 20 °C)	log P_{ow}	pKa	Vapor pressure (mm Hg at 20 °C)	Ref.
E1	$C_{18}H_{22}O_2$	53-16-7	270.4	12.4	3.43	10.8	2.3×10^{-10}	Lai et al. (2000), Tabak et al. (1981)
E2	$C_{18}H_{24}O_2$	50-28-2	272.4	12.9	3.94	10.5	2.3×10^{-10}	Lai et al. (2000), Tabak et al. (1981)
E3	$C_{18}H_{24}O_3$	50-27-1	288.4	13.2	2.81	10.4	6.7×10^{-15}	Lai et al. (2000), Tabak et al. (1981)
EE2	$C_{20}H_{24}O_2$	57-63-6	296.4	4.8	4.15	10.2	4.5×10^{-11}	Kim (2009)

CAS = Chemical Abstracts Service
γ_{sat} = Solubility in water
K_{ow} = Octanol/water partition coefficient
Ka = Acid dissociation constant

electron-deficient carbon atom of the carbonyl groups can function as electron acceptors (Ahmed et al., 2018; Peiris et al., 2017). In contrast, the carboxyl groups (pKa = 5–6.4) present on the BC surface can function as π acceptors only when the carboxyl groups are protonated at a pH < pKa (Ahmed et al., 2018; Peiris et al., 2017). Consequently, a BC surface that is rich in carboxyl and carbonyl groups can become a potential adsorbent for estrogens under mildly acidic conditions (pH 3–6). In contrast to low-temperature BC (LTBC), high- temperature BC (HTBC) has an extensively graphitized surface that enables it to act as a donor (Peiris et al., 2017; Rajapaksha et al., 2014).

Estrogen uptake by BC has been reported to take place via several mechanisms (Ahmed et al., 2018; Dong et al., 2018; Han et al., 2016; Liu et al., 2019b; Regkouzas and Diamadopoulos, 2019). In a majority of the studies conducted, π – π electron-donor acceptor (EDA) interactions are considered as the dominant mechanism of estrogen uptake (Ahmed et al., 2018; Dong et al., 2018; Tian et al., 2018; Yin et al., 2018). Generally, EDA interactions take place in between the phenolic moiety of estrogen and the electron-accepting moieties attached to BC (Liu

et al., 2019b; Tao et al., 2019; Tian et al., 2018). However, Ahmed et al. have reported EDA interactions between positively charged estrogens and the BC surface (Ahmed et al., 2018). Hydrogen bonding (H-bonding) is another mechanism that has been identified as operating between the phenolic and hydroxyl groups of the estrogens and the O-SFGs present on the BC surface (Ahmed et al., 2018; Han et al., 2016; Tian et al., 2018).

Another mechanism that has been reported is the electrostatic force of attraction that arises between the phenolate ion of the estrogen and the positively charged BC surface (pH < pH$_{PZC}$ of BC) (Liu et al., 2019a, 2019b; Tao et al., 2019). Furthermore, charge assisted hydrogen bonding (CAHB) has been suggested as a possible mechanism when both the adsorbate and the adsorbent surfaces are negatively charged (Ahmed et al., 2018). Charge assisted hydrogen bonding can result when a proton is abstracted from water in the medium to facilitate the formation of H-bonds between estrogen and BC (Ahmed et al., 2017, 2018). It can be seen that when both the estrogen and BC surface carry the same charge, electrostatic repulsion can restrict adsorption. However, amidst the

repulsive forces that operate, the limited sorption capacity observed has been attributed to hydrophobic interactions and pore-filling (Ahmed et al., 2018; Han et al., 2016; Kim et al., 2016; Liu et al., 2019b; Regkouzas and Diamadopoulos, 2019; Tao et al., 2019).

Sorptive mechanisms depend on the surface charge of BC and the speciation of estrogen. Electron donor acceptor interactions can occur in two different ways with undissociated estrogens. The resonance stabilized undissociated estrogens create an electron-rich aromatic ring structure that can act as an electron donor. The carboxylic moieties in the BC can create an electron-deficient region on the graphitic surface that can act as an electron acceptor. Therefore, EDA interactions form between the adsorbent and adsorbate. Secondly, at extremely acidic pH conditions (pH < 2), the estrogen will possess a positive charge and the rings of the BC will act as electron donors.

Another possible mechanism that can take place between the dissociated estrogen and positively charged BC is electrostatic interactions. Hydrogen bonding can take place between the OH groups of estrogens, and the oxygen and nitrogen-containing groups on the BC surface. However, at high pH (pH > 10), CAHB interactions can take place between the dissociated estrogen and negatively charged BC surface even though electrostatic repulsion restricts sorptive removal. A graphical representation of the reported adsorptive mechanisms is shown in Fig. 2.

3.2. Effect of feedstock and production conditions

Literature provides conclusive evidence for the relation between the feedstock type used and adsorption capacity (Wang et al., 2016; Zhou et al., 2016). The physicochemical properties of BC can vary depending on whether the feedstock type used is plant-based or animal-based.

In one study, swine manure, maize straw and pinewood BC

pyrolyzed at seven different temperatures were used for the adsorption of EE2. The swine manure derived BC had the highest adsorption capacity because of its high ash content, constituting primarily of phosphates and calcium oxides, which can enhance the surface polarity of the BC (Wang et al., 2016). Zhou et al. used wheat straw and peanut shell (350–500 °C) BC and observed an increase in capacity for wheat straw-based BC at low equilibrium concentrations. The wheat straw-BC had more surface functional groups than the peanut shell-based BC, facilitating the formation of H-bonds. At high concentrations, however, peanut shell-based BC had higher capacities due to its high surface area (Zhou et al., 2016).

Dominant sorption mechanisms can vary with pyrolysis temperature. With HTBC, adsorption was boosted by EDA interactions occurring between the estrogens and the highly graphitized BC surface (Wang et al., 2016, 2017). In contrast, LTBC had more O-SFGs resulting in H-bonding (Dong et al., 2018). Furthermore, some authors have utilized hydrochars from hydrothermal carbonization for estrogen adsorption (Han et al., 2016; Sun et al., 2011).

Sun et al. reported higher adsorption capacities for EE2 due to an increase in O-SFGs on the hydrochar produced from poultry litter and swine solids as compared to the pyrochars. Moreover, the elevated O/C ratios suggested that more H-bonding and electrostatic interactions existed between EE2 and the hydrochars, compared to pyrochars produced using poultry litter and wheat straw (Sun et al., 2011). The increased polarity of the hydrochar is believed to be due to the low pyrolysis temperature and type of biomass used e.g. using wet biomass. Contrastingly, another study reported that hydrochars were found to have a lower polarity index, making it more hydrophobic than the pyrochar. An increase in aryl and alkyl moieties on the hydrochar surface contributed to E1 adsorption via hydrophobic interactions (Han
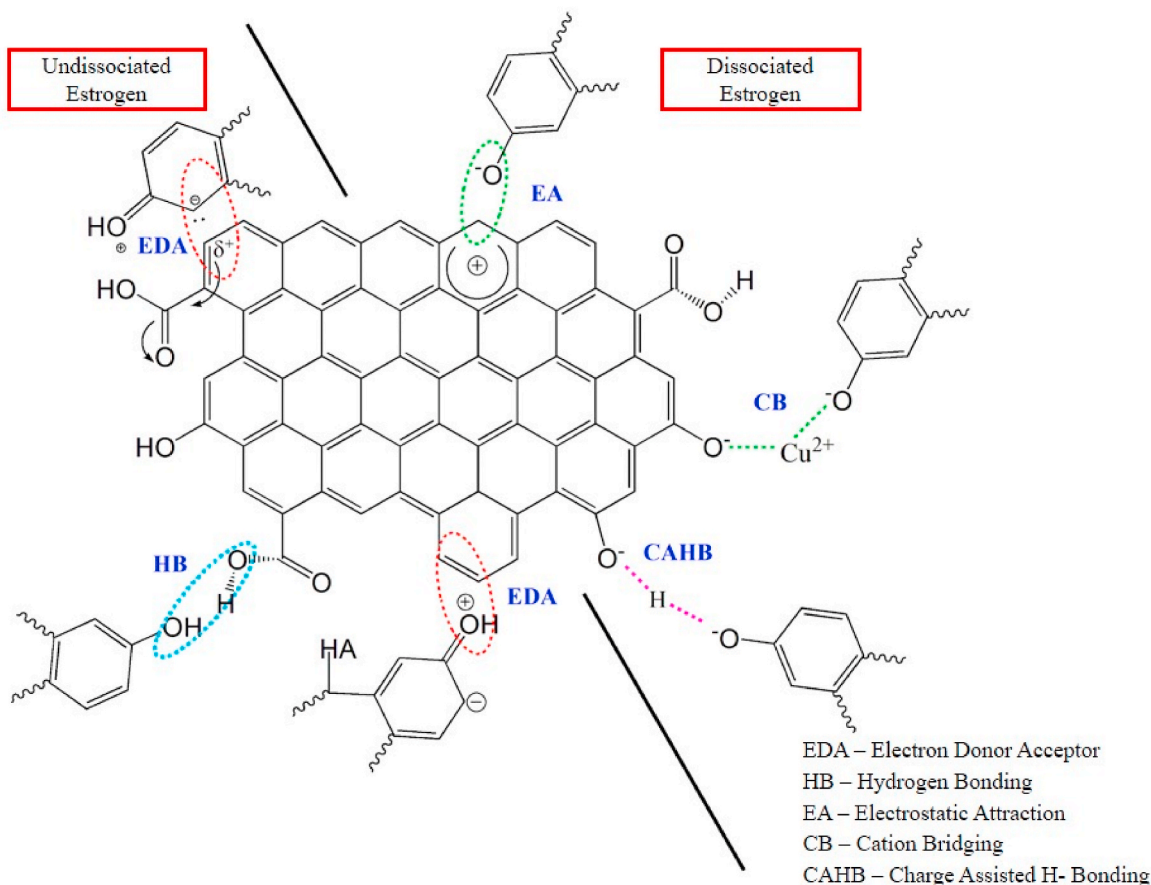

Fig. 2. Graphical illustration of adsorption mechanisms during the adsorption of steroidal estrogens onto biochar surfaces.

et al., 2016). Therefore, it can be inferred that the three variables, feedstock, pyrolysis conditions (atmosphere and time), and pyrolysis temperature are significant factors that contribute to the adsorption process.

3.3. Effect of pH on steroidal estrogen sorption

Estrogen-BC adsorption capacities are known to vary with pH. For the convenience of discussing the influence of pH on estrogen sorption, the authors have identified four major patterns which were deduced on the basis of surface charge, estrogen speciation and working pH. The first pattern was more commonly reported and was observed for E2 and EE2 adsorption. The adsorption capacities remained stable over the pH range of 3–9, and above pH 9 the capacities showed a decrease (Liu et al., 2019b, 2020b; Ning et al., 2017; Tian et al., 2018). The studies which gave this pattern used montmorillonite/hydrochar, montmorillonite/carboxymethyl cellulose BC, lotus seedpod BC (pristine and modified) and a Fe–Mn hydrochar nanocomposite for estrogen uptake. Authors Tian et al. and Liu et al. attributed the capacities of montmorillonite incorporated BCs in the stabilized region from pH 3–9 to H-bonding (Liu et al., 2019b; Tian et al., 2018). The decreasing capacities at pH > 9 were mainly due to electrostatic repulsion, although Tian et al. considered the competitive effect by hydroxyl ions in the medium as an additional factor that contributed to the observed capacity decrease (Liu et al., 2019b; Ning et al., 2017; Tian et al., 2018). Furthermore, Liu et al. stated that the driving force for adsorption at high pH was pore filling or van der Waals forces (Liu et al., 2019b). Contrarily, a study that used graphene oxide activated magnetic BC showed an increase in adsorption capacities above pH 10, after having a stable capacity from pH 3–10. The increase in adsorption capacity after pH 10 is attributed to the electrostatic attractions formed between the positively charged BC surface and the negatively charged estrogen species (Liu et al., 2019a).

A second pattern that was evident in literature was the gradual decrease in capacity with increasing pH (reportedly from pH 3–11) (Liu et al., 2019b; Tao et al., 2019). Tao et al. made this observation for BC derived from the fruit plant *Litchi chinensis Sonn* orchard. At low pH, the high capacities observed for raw and modified BC were due to the protonation of the BC surface which led to the creation of more positive sites. This enabled more of the molecular estrogens to bind on the BC surface. Upon impregnating the BC with calcium and Fe–Mn, the variation of capacity with pH reduced. This reduction was due to the reaction of H_3O^+ with $CaCO_3$ and Fe–Mn binary oxide present on the BC surface (Tao et al., 2019). Moreover, the increased surface area upon modification reduced the competitive effect between E1 and H_3O^+ at low pH, leading to comparatively higher capacities under acidic conditions. In another study, Yin et al. observed a similar pattern as Tao et al. for the adsorption of E2 using an attapulgite/BC nanocomposite. The authors presumed that this pattern could be due to the negative zeta potential of the BC surface, which decreased with increasing pH (Yin et al., 2019). In another study that used rice straw BC for E2 adsorption, Wang et al. reported stabilized capacities from pH 3 to 7, a sharp decrease thereafter from pH 7 to 8 and then a gradual decrease from pH 8 to 12. The authors have ascribed this observation to the changes in surface charge and E2 speciation (Wang et al., 2017).

A third pattern was identified, showing a gradual increase, followed by a decrease in adsorption capacity with increasing pH. The sorptive uptake of E2 using montmorillonite incorporated cow manure and wheat straw BC gave increasing E2 capacities from pH 3–9 and showed a sharp decrease thereafter from pH 9–11. The authors stated that the capacity increase was governed by H-bonding between the hydroxyl group of the estrogen and the BC surface. With increasing pH (when pH > pKa), the H-bonding was weakened due to ionization of the estrogen molecules. Moreover, repulsive electronic forces at elevated pH resulted in a capacity decrease as well (Tong et al., 2020).

A final adsorption capacity vs pH pattern took a zig-zag shape with distinctive maxima and minima (Ahmed et al., 2018; Yin et al., 2018). The observation was made for the adsorption of E1, E2, E3 and EE2 by Ahmed and Yin et al. Going from pH 2–3, Yin et al. reported a decrease in capacity for E2 due to electrostatic repulsion as a result of the $FeOH_2^+$ on the activated magnetic rice straw BC surface (pH_{PZC} = 3.25–6.26) and the protonated E2. A capacity increase from pH 3–7 was attributed to strong H-bonding, electrostatic and EDA interactions between the BC and E2. With further increase in pH, the electronic repulsions between the negatively charged BC and E2 caused the capacity to decrease (Yin et al., 2018).

The invasive plant species, Tasmanian blue gum (*Eucalyptus Globulus*), was utilized by Ahmed et al. to prepare a phosphoric modified BC which showed a similar pH variation as Yin et al. However, the observed maxima occurred at different pH (Ahmed et al., 2018). The low capacity at pH 1.85 was due to the electrostatic repulsion between the positively charged BC and E2. The sorption at this pH was attributed to EDA interactions. At pH 3 and 8 where the adsorption maxima were observed, H-bonding, CAHB, and EDA were in operation. The highest maximum was observed at pH 3 and was governed predominantly by the EDA mechanism. The second maximum at pH 8 was due to H-bonding and was not as high as pH 3 because of the repulsive forces that were starting to act between the estrogen and BC surface (pKa of the phenolic group = 8–10). The decreasing capacities observed by Ahmed et al. after pH 9 were due to repulsive forces (Ahmed et al., 2018).

The fact that estrogens retain their undissociated form at pH < pKa was supported by the minimal capacity variations observed by several authors. The pH-dependent distribution coefficient, D, was used as a more realistic representation of the adsorption of E2 onto both the raw and modified BC types used (Dong et al., 2018; Jung et al., 2013; Kim et al., 2016). Overall, it can be inferred that the sorptive removal of estrogens from aqueous systems is favored within a pH range of 3–8. As estrogens exist in the unionized form within this range, EDA and H-bonding interactions will serve as the main driving force for the adsorption process.

3.4. Effect of matrix components

Sorptive uptake of estrogens from natural water systems is influenced by the different matrix components such as natural organic matter (NOM), background electrolytes and co-existing metal ions. Natural organic matter is an abundant constituent in surface and groundwater. Typically, NOM carries an overall negative charge owing to the many carboxyl and phenolic moieties in its structure (Bhatnagar and Sillanpää, 2017; Jiang et al., 2017; Liu et al., 2020b). As 70% of NOM is comprised of humic acids (HA), many authors have used HA to investigate matrix interferences in simulated laboratory water samples (Ning et al., 2017; Qu et al., 2018). Furthermore, organic acid ligands and fulvic acids have been used to simulate natural water matrices as well (Jiang et al., 2017; Liu et al., 2019a). Natural organic matter can influence adsorption in two ways, either by exhibiting a negligible competitive effect or by forming interactions that significantly reduce the removal of estrogen.

Firstly, it has been observed by several authors that for E2 and EE2, the presence of NOM in the medium did not lead to a substantial variation in adsorption capacity (Dong et al., 2018; Jung et al., 2013; Kim et al., 2016; Liu et al., 2020a, 2020b; Reguyal and Sarmah, 2018). Several interactions have been proposed for this observation. In one study, it was claimed that the bulky NOM molecules experienced steric hindrance, making it difficult for the functional groups on NOM to interact with the BC active sites. The surface functional groups on the BC surface were, therefore, available for binding with E2 and the capacities were not observed to change significantly. Furthermore, it was stated that at concentrations as low as 10 ppm, adsorption of E2 onto NOM was low and that E2 was readily available to bind with the BC (Liu et al., 2020b). In a second study, the complexation of E2 and NOM reportedly led to stabilized capacities and the NOM-E2 complex that formed was

adsorbed onto the BC via strong π interactions (Liu et al., 2020a).

The second observation reported in literature was that adsorption capacities significantly decreased in the presence of NOM (Jiang et al., 2017; Liu et al., 2019a; Ning et al., 2017; Regkouzas and Diamadopoulos, 2019; Tao et al., 2019; Wang et al., 2017). The decreasing adsorption trend was ascribed to the interactions between (1) NOM and estrogen and (2) NOM and BC. Wang et al. and Liu et al. have observed that NOM can bond directly with estrogens in the medium, making the estrogens less available for the binding sites on the BC surface (Liu et al., 2019a; Wang et al., 2017). Interactions between NOM and BC can influence sorption in two contrasting ways. The NOM can directly compete with the binding sites on the BC. In the case where oxalic acid and benzoic acid were used, it was observed that the oxalic acid ligand inhibited the uptake of E2 onto graphene oxide supported activated magnetic BC as the polar functional groups on the BC surface selectively favored interacting with the carboxyls of the oxalic acid ligand (Liu et al., 2019a).

Decreased adsorption capacities are also observed due to the polar functionalities that are created on the BC surface after bonding with NOM. These functional groups promote the formation of water clusters around the BC surface via an extensive H-bonding network. As a result, the BC will lose its hydrophobicity and hence, its ability to adsorb estrogens via hydrophobic interactions (Ning et al., 2017; Tao et al., 2019). Moreover, pore-blocking was reported to take place in the presence of HA, which reduced the available binding sites for E2 and EE2 uptake (Jiang et al., 2017; Ning et al., 2017; Yin et al., 2019). It has been reported that the presence of NOM prevents the uptake of estrogen due to micropore blocking (Newcombe et al., 2002). Therefore, it can be inferred that the influence exerted by NOM towards estrogen uptake is dependent upon the surface morphology and functionality of the BC.

Ionic species in the medium are reported to influence adsorption in three ways: 1) salting out, 2) squeezing out and 3) screening effects. Salting-out takes place when ionic species interact with water molecules, resulting in the activity coefficient of the hydrophobic solutes to increase. As a result, the solubility of such solutes is reduced (Han et al., 2013; Kalra et al., 2001; Kim et al., 2016; Ning et al., 2017; Yin et al., 2019). The interactions that ions make with hydrophobic solutes are dependent upon the concentration and charge density of the ions, molecular size and molecular geometry of the hydrophobic solute. When the charge density of an ion is high, it will preferentially interact with water over the hydrophobic solute, thereby decreasing the solute's solubility (Kalra et al., 2001). A study presented by Xie et al. provided justification for this observation, and implied that salting-out enhanced the hydrophobicity of the organic solutes alongside the partition coefficient (Xie et al., 1997). As a result, the ability of solutes to bind to BC via hydrophobic interactions increased. Therefore, the salting-out process can be considered as a favorable mechanism for estrogen adsorption onto BC (Liu et al., 2019a; Yin et al., 2019).

The squeezing out effect is another phenomenon that promotes the aggregation of BC particles. Ions present in the medium can penetrate the diffuse double layer surrounding the BC surface and make the layer smaller and more dense (Zhang et al., 2010). Aggregation of BC reduced the number of available binding sites for estrogen adsorption (Dong et al., 2018; López-Ramón et al., 2003; Wang et al., 2017). The screening effect, however, depends on the surface charge and the type of interactions that occur between the BC and the adsorbate. If the BC or analyte is ionized, electrostatic attractions can exist between the two species. When external ionic species are introduced to the medium, these ions can place themselves between the BC and analyte, thereby decreasing the attractive electrostatic forces (López-Ramón et al., 2003; Peiris et al., 2017; Wang et al., 2017). The ionic species that have been frequently utilized are calcium chloride and sodium chloride.

Ionic strength is known to affect the adsorption capacities of estrogens in three disparate ways. In majority of the literature, an increase in ionic strength is known to cause an increase in adsorption capacity (Dong et al., 2018; Ning et al., 2017; Rovani et al., 2019; Tao et al., 2019;

Wang et al., 2017). Wang et al., observed a sharp increase in capacity for E2 when the concentration of NaCl was raised from 0 to 0.01 M. Thereafter, adsorption capacities increased only gradually until 0.1 M. The sharp increase was ascribed to the salting-out effect, whereas the gradual increase was related to the squeezing out effect (Dong et al., 2018; Liu et al., 2020a; Wang et al., 2017). A minimal increase in E2 uptake was observed for the hydrochar/Fe–Mn binary oxide nanocomposite, and this limited enhancement was reported due to screening and salting-out effects (Ning et al., 2017).

Secondly, increasing ionic strength can also result in a decrease in adsorption capacity. Liu et al. observed that E2 removal capacities for KOH modified lotus seed pod BC decreased due to the squeezing-out effect (Liu et al., 2020b). A similar pattern was observed by Rovani et al., when BC loaded SPE cartridges were used for the removal of E2. When the concentration of NaCl increased, the percentage recovery of the SPE syringe was observed to decrease. This has been attributed to the formation of π^+- π interactions between the cations in the medium and the electron-donating arene surface, which reduced the available binding sites for BC-E2 interactions (Rovani et al., 2019).

The third pattern showed both a gradual decrease and an increase in capacities with pH. This observation was made for E2 removal using raw, activated magnetic BC and graphene oxide impregnated activated magnetic BC. The E2 uptake by the three adsorbents decreased at low concentrations as a result of the squeezing out effect. However, further increasing the concentration caused an increase in capacity due to the salting-out effect (Liu et al., 2019a). However, Tong et al. observed that the effect of ionic strength on E2 adsorption capacities was negligible owing to the weak salting-out effect (Tong et al., 2020).

Mono-, di-, and trivalent species in the medium have been found to affect steroidal estrogen uptake in several ways. Monovalent cations have been reported to favor E2 removal more than divalent cations (Kim et al., 2016; Yin et al., 2019). Kim et al. have reported that the salting-out effect by monovalent ions can lead to high adsorption capacities (Kim et al., 2016). However, Yin et al. and Kim et al. state that the squeezing out effect and the ability of divalent cations to form complexes with E2 prior to adsorption are possibilities for the observed lower adsorption capacities of E2 (Kim et al., 2016; Yin et al., 2019). However, Wang et al. have observed an increase in capacity with the addition of divalent than monovalent cations (Wang et al., 2017). The forces of attraction between the divalent cations and the negatively charged BC surface is conducive for the formation of E2 complexes.

The existence of trivalent anions resulted in better adsorption capacity than mono- and divalent anions (Wang et al., 2017). On the contrary, a few authors have reported that the effect of cations and anions on capacity were negligible due to the repulsion between the negatively charged BC surface and the anions (Tong et al., 2020; Yin et al., 2019). However, Liu et al. observed that there was a slight inhibition in uptake due to the competitive effect of the sulfate ions (Liu et al., 2020a).

The effect of copper ions on the adsorption of E2 has been investigated. When the copper concentration was increased from 0 to 20 ppm, the adsorption capacity was seen to increase as well. Thereafter, the capacity decreased upon increasing the concentration to 60 ppm. The uptake of copper and E2 depended on the interactions between the surface functional groups and the porous structure of the BC. At low concentrations, the repulsive forces between the negatively charged BC and E2 were mitigated by the cationic bridging effect caused by the complexation of BC- E2- Cu or BC-Cu-E2, which led to an increase in E2 adsorption. At high concentrations of Cu^{2+}, competition exists between E2 and Cu^{2+} for the pores of the BC, which led to a decrease in adsorption (Yin et al., 2018).

The influence of surfactants, Al_2O_3 nanoparticles and microplastics on estrogen removal has been investigated by Yin et al., Liu et al. and Ahmed et al. (Ahmed et al., 2017; Liu et al., 2020a; Yin et al., 2019). Sorption capacities were seen to decrease in the presence of surfactants in both the experiments (Ahmed et al., 2018; Yin et al., 2019). Yin et al.

reported that highly soluble surfactants increased the solubility of E2 and therefore, inhibited E2 uptake (Yin et al., 2019). In the study conducted by Ahmed et al., samples were spiked with the surfactants, sodium lauryl sulfonate and acacia gum, and it was observed that the adsorption of E1, E2, E3 and EE2, was reduced. It was suggested that the surfactants competed with the estrogens for the functional groups on the BC surface (Ahmed et al., 2018). The presence of both Al_2O_3 nanoparticles and microplastics led to a faster equilibrium, which was attributed to the additional binding sites that formed on the BC upon incorporating Al_2O_3 nanoparticles and microplastics (Liu et al., 2020a).

3.5. Value added biochar for enhanced estrogen removal

Engineered BC has been prepared via surface acidification, basification, magnetization, and metal ion impregnation for aqueous estrogen remediation. These modifications significantly influence the surface area and functional groups on the BC surface, thereby leading to enhanced adsorption capacities.

Inorganic acids and bases are frequently used to produce engineered BC (Liu et al., 2020a, 2020b; Tao et al., 2019). When considering estrogen adsorption, a post-acid modification using orthophosphoric acid has been reported by Ahmed et al. on *Eucalyptus globulus* wood particle derived BC for the removal of E1, E2, E3, and EE2. The modification resulted in many mesopores and macropores that had pore diameters compatible with estrogen molecules. This facilitated estrogen uptake via pore filling. In addition to the O-SFGs such as carboxylic, hydroxyl, and carbonyl, XPS data revealed the presence of pentavalent tetra-coordinated phosphorus moieties on the BC surface. The resultant BC was, therefore, rich in polar groups and contributed to the uptake of estrogens through electrostatic interactions and H- bonding. Moreover, the functionalized BC surface was found to have aromatic carbon chains that enabled the formation of EDA interactions (Ahmed et al., 2018).

Base modifications were conducted by Kim et al. and Liu et al. using sodium hydroxide and potassium hydroxide respectively (Kim et al., 2016; Liu et al., 2020b). Kim et al. have observed an increase in surface area and polar moieties, such as O-alkyl, carboxyl carbons and methoxyl upon pre-modification. These groups enabled better π-hydrogen bonding and induced electrostatic interactions between E2 and BC (Kim et al., 2016). In the investigation conducted by Liu et al., pre, direct, and post modified lotus seed pod BC was produced using KOH. There was a tenfold increase in the surface area after each type of modification. However, amongst the three KOH modifications done, the post-modification gave the highest E2 uptake as it imparted the highest surface area to the lotus seed pod BC. The increase in the surface area upon base modification could be due to the removal of ash content, destruction of the aromatic structure of the BC, or shrinkage of pores. The extent of pore shrinkage was dependent on the type of base treatment used (Yakout et al., 2015). The amine functionalities and aromatic carbons that are formed upon modification were presumed to influence electrostatic attractions and EDA interactions, resulting in higher E2 capacities after modification (Liu et al., 2020b).

Magnetization is a value addition incorporated for the easy recovery of the exhausted BC. In literature, magnetically modified BCs have been utilized by authors for the adsorption of E2 (Dong et al., 2018; Liu et al., 2019a; Yin et al., 2018). A magnetic modification typically results in the deposition of Fe particles on the BC surface, providing additional binding sites for estrogen uptake. In their research using rice straw derived BC, Yin et al. and Liu et al. carried out a one-step synthesis that resulted in both BC activation and magnetization. For the purpose of activating the BC, Yin et al. used zinc chloride whereas Liu et al. used potassium carbonate. Magnetization was done using iron (iii) chloride hexahydrate. In both the studies, E2 capacities were increased upon modification owing to the increased surface area and functional groups. The surface area and functional groups were reported to increase as a collective result of the activation and magnetization processes (Liu et al., 2019a; Yin et al., 2018). After producing the activated magnetic BC

(AMBC), Liu et al. went on to incorporate graphene oxide to the structure (GO-AMBC), which gave a fourfold increase in surface area as compared to the AMBC. Between zinc chloride and potassium carbonate activations, zinc chloride yielded the highest adsorption capacity, which was even greater than the capacity observed by Liu et al. for GO-AMBC. The reason for the latter observation was that the surface area of the $ZnCl_2$ AMBC was 1.5 fold higher than the GO-AMBC. In another study, magnetization has also been carried out for lotus seed pod BC using potassium ferrate. The strong oxidizing ability of potassium ferrate was thought to result in graphitic carbon and Fe_3C species, alongside increased BC surface area. The enhanced graphitic nature and surface area upon potassium ferrate modification made it conducive for E2 adsorption (Liu et al., 2020a).

Metallic impregnation has been carried out by Tao et al. and Ning et al. for the adsorption of E1 and E2, respectively. The Fe–Mn binary oxide loading was used by both authors, and it was observed that there was an increase in surface area (Ning et al., 2017; Tao et al., 2019; Xie et al., 2015; Zhang et al., 2014) due to the (1) amorphous nature of the Fe particles and (2) the potential of Fe and Mn species to undergo redox reactions with the BC surface functional groups (Tao et al., 2019). Tao et al. have produced calcium impregnation as well and suggested that, in addition to the other surface functionalities such as C–O and C–C═O on the BC surface, the presence of Ca^{2+} in Ca-BC and Fe/Mn oxides in the Fe-Mn-BC provided more binding sites for the adsorption of E1 (Tao et al., 2019).

3.6. Adsorption isotherms for estrogen-biochar equilibrium

Adsorption isotherms describe the equilibrium distribution of an analyte between the adsorbent surface and the aqueous medium. Isotherms for adsorption in aqueous media reveal important information regarding the sorption mechanisms taking place at a solid-liquid interface. Estrogen removal using BC has been modeled using the Langmuir, Freundlich, Langmuir-Freundlich, Dubinin-Radushkevich, Temkin, Redlich Peterson, and Polanyi Manes models. Amongst these, the Freundlich model and Langmuir models were the most commonly reported. The Freundlich model showed best fits for E1, E2, E3, and EE2, suggesting heterogeneous adsorption on BC surfaces (Jung et al., 2013; Kim et al., 2016; Liu et al., 2019b, 2020b; Peterson et al., 2013; Sun et al., 2011; Tong et al., 2020; Wang et al., 2017; Zhou et al., 2016). The Langmuir isotherm model was best fitted for estrogen adsorption onto rice straw BC, graphene-like magnetic BC, bagasse BC, functionalized BC, modified *Litchi chinesis* Sonn BC, and activated magnetic BC, indicating homogenous surface adsorption (Ahmed et al., 2018; Dong et al., 2018; Liu et al., 2020a; Tong et al., 2020; Yin et al., 2019) Contrastingly, Ning et al. and Tong et al. observed that the adsorption of E2 is well described by both the Langmuir and Freundlich models, signifying that there were multiple mechanisms involved (Ning et al., 2017; Tong et al., 2020).

In these studies, both non-linear and linear isotherm models have been utilized by authors to depict the adsorption process. The parameter 'n' is known as adsorption intensity and provides a measure for the deviation from linearity for the adsorption process (Wibowo et al., 2017). The favorability of adsorption is generally classified with the values of n_F: good (2–10), moderately difficult (1–2), and poor (<1). When n = 1, the isotherm is considered linear. The shape of the isotherm curve is nearly independent of the rate-determining mechanism for the adsorption (Navarathna et al., 2019; Sun et al., 2013). In BCs subjected to different pyrolysis conditions and value additions, the non-linearity observed was ascribed to the aromatic domains, increased porosity, and surface area of the BC (Sun et al., 2011; Tao et al., 2019; Wang et al., 2016; Yin et al., 2018). In a single solute sorption study conducted by Tong et al., the adsorption of E2 and EE2 was described as taking place on different carbonized and non-carbonized portions of the BC. The more polar EE2 underwent linear partitioning on the polar, functionalized BC fraction and the non-polar E2 molecules partitioned to the

non-polar char fraction (Tong et al., 2019a; Zhou et al., 2016). In some cases, the favorability of an adsorption is also evaluated using the dimensionless separation factor R_L. When the R_L values are in the range $0 < R_L < 1$, the sorption process is considered to be favorable (Patel et al., 2015; Sun et al., 2013).

For the effective implementation of BC in field applications, it is crucial to evaluate the temperature dependency of adsorption. The Vant Hoff's and Clausius Clapeyron equations have been employed in studies to determine thermodynamic parameters such as enthalpy, entropy, Gibbs free energy, and isosteric heat of adsorption. In the reported studies, thermodynamic parameters have been evaluated mainly for the adsorption of E2 and EE2. Several authors have provided evidence to support that the adsorption of E2 onto bagasse derived, rice straw derived, and graphene oxide supported magnetic BC was a spontaneous, exothermic process that resulted in decreased randomness on the solid-liquid interface (Dong et al., 2018; Yin et al., 2019). However, Tong et al. observed that the adsorption of E2 and EE2 on biosolid derived BC was an endothermic process that resulted in a positive entropy change. Tong et al. suggested that energy was absorbed from the surroundings to overcome interactions with water molecules in the system and to promote chemisorption on to the BC surface. Furthermore, the authors stated that the structure of the bio-solid derived BC facilitated non-specific hydrophobic interactions between the estrogens and BC surface, which led to the high values of entropy observed (Tong et al., 2019a). Another thermodynamic parameter evaluated was the isosteric heat capacity, which is defined as the differential heat of adsorption at a fixed surface loading (Tong et al., 2019a). The parameter supports the presence of heterogeneous sites on an adsorbent. The lower isosteric heats observed for the adsorption of EE2 and E2 with increasing concentration suggests that higher affinity adsorption sites on the BC are occupied first, giving high isosteric heat values. In contrast, with increasing analyte concentration, the low-affinity sites are filled, causing the isosteric heat to decrease. The parameters of the reported isotherm models are shown in Table S1.

3.7. Kinetics of steroidal estrogen adsorption

The adsorption kinetic models that have been commonly employed for estrogen sorption are pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, Weber Morris intraparticle diffusion (IPD), external mass transfer model, and Boyd model (Ahmed et al., 2018; Dong et al., 2018; Liu et al., 2019b, 2020a; Sun et al., 2011; Tong et al., 2020; Wang et al., 2017). The PFO and PSO models are helpful in determining the rate of adsorption and provides useful insight into the chemisorptive and physisorptive nature of adsorption. Moreover, the PSO model can be used to deduce the parameter 'h', which is an indication of the initial rate of adsorption. The Elovich, IPD, external mass transfer model, and Boyd models have been used to decide the rate determining step (RDS) (Peiris et al., 2017).

A majority of the authors have observed that the estrogen adsorption capacities were best fitted for the PSO model (Dong et al., 2018; Liu et al., 2019b; Ning et al., 2017; Regkouzas and Diamadopoulos, 2019; Tong et al., 2020). Hence, it provides evidence for chemisorptive adsorption.

Within short contact times, Dong et al. observed that E2 became saturated on the magnetic BC nanoparticles (Mag-BCNP). This was due to the rapid and easy access of E2 into the nanoscale porous structure of the BC (Dong et al., 2018). Dong et al. used the PSO initial rate of adsorption 'h', which provides information on E2 uptake when the concentration is equal to the initial concentration of E2 added at time→0. Higher 'h' values were observed for Mag-BCNP that were produced at 600 and 800 °C as compared to 400 °C. The high 'h' values observed can be attributed to the high density of binding sites on both the adsorbent and adsorbate (Sun et al., 2014; Zhang et al., 2013). Additionally, Dong et al. reported that the driving force for high 'h' values were π - interactions and H-bonding, which facilitated E2 to overcome resistance to mass transfer (Dong et al., 2018). Contrastingly, out of the PSO, PFO, Elovich, and Ritchie models fitted, Liu et al. obtained the highest regression for the Ritchie n^{th} model, suggesting multiple mechanisms (Liu et al., 2019b).

Several authors have utilized the IPD to investigate the precise mechanism of the RDS. The IPD graphs had multilinearities over the entire time range studied and were not seen to pass through the origin. Authors state that this observation was due to the contribution of both boundary layer diffusion and IPD to the RDS (Ahmed et al., 2018; Ning et al., 2017; Tong et al., 2020; Wang et al., 2017; Yin et al., 2018, 2019). To resolve between the two steps and to determine the exact RDS, the external mass transfer model and the Boyd model were utilized. Ahmed et al. claimed that external mass transfer played a significant role in the competitive sorption of E1, E2, E3, and EE2 onto functionalized BC. As evidenced by the high regression coefficients ($R^2 > 0.950$) that were obtained, boundary layer diffusion was deduced as the mechanism that governed the sorption process (Akkaya and Özer, 2005; Zhang et al., 2013). The RDS was further established using the Boyd Model. If the graph passes through the origin, the RDS is considered as IPD. A graph that does not pass through the origin indicates that film diffusion is limiting the rate of adsorption.

In a competitive sorption study, Ahmed et al. observed the RDS to be boundary layer diffusion. Hence, it was deduced that competitive sorption onto functionalized BC took place via an intricate mechanism that involved both boundary layer diffusion and electron exchange. A similar observation was made by Wang et al. for rice straw BC using only the Boyd's plot. The parameters of the reported kinetic models are shown in Table S1.

3.8. Competitive sorption of estrogens

Competitive sorption studies have been carried out to investigate the influence of coexisting micropollutants on the sorptive uptake of estrogens. Molecular size and hydrophobicity are considered as contributing factors for competitive sorption (Peiris et al., 2017). Reguyal et al. studied the competitive sorption of the antibiotic sulfamethoxazole (SMX) and EE2 by pine sawdust derived BC. Even though the presence of SMX did not affect the sorptive uptake of EE2, the presence of EE2 inhibited the adsorption of SMX. The higher hydrophobicity of the EE2 facilitated greater EDA interactions with the BC and EE2 than with SMX, creating a competition (Jung et al., 2013; Reguyal and Sarmah, 2018). Ahmed et al. observed enhanced sorption for E1, E2, E3, and EE2 compared to bisphenol A (BPA), and 4-tert-butylphenol due to the high hydrophobicity of estrogens (Ahmed et al., 2018). Estrone was found to exhibit the highest adsorption capacity among the estrogens, owing to the presence of the carbonyl group which favored the formation of EDA interactions (Ahmed et al., 2018).

In a study conducted to evaluate the removal of EE2, BPA, and carbamazepine (CBZ) using nitrogen and oxygen functionalized BC, it was observed that the EE2 removal was not restricted by the other EDC. The undissociated form of EE2 was reported to govern the adsorption throughout a wide pH range via hydrophobic interactions, compared to BPA and CBZ. Moreover, the presence of aromatic groups promoted EDA interaction. However, in the presence of hydrophobic EE2, the uptake of atrazine was inhibited (Jung et al., 2013). A concise representation of the reported literature is given in Table S2.

3.9. Catalytic activity of biochar for estrogen degradation

In addition to the sorptive properties of BC, the catalytic degradation potency of BC has also been reported. The catalytic activity of BC is due to the presence of persistent free radicals (PFR) on the BC surface. Persistent free radicals are formed during pyrolysis and are assisted by the sp^2 carbon array, surface functional groups and heteroatoms present on the BC (Fang et al., 2014, 2015). Metal atoms added during composite formation can also contribute to PFR formation. During pyrolysis,

the phenolic groups of the biomass can act as precursors for the formation of PFRs. Oxygen-centered PFRs usually form at relatively low pyrolysis temperatures, and during a short pyrolysis time. When subjected to high temperatures for longer time periods, oxygen-centered PFRs decompose and convert to carbon-centered PFRs (Fang et al., 2015). The formation of surface-bound PFRs is accompanied by electron transfer from phenolic moieties to metal atoms owing to the double effect of transitional metals (Fang et al., 2014). Delocalized electrons in the graphene rings promote the formation of PFRs due to resonance stabilization (Fang et al., 2015; Ruan et al., 2019).

In one study, Yu et al. utilized an iron–hydrochar composite derived from pinewood for the removal of E1, E2, and E3 with the aid of H_2O_2. The carbon-centered PFRs formed during the pyrolysis, converted the dissolved $^\bullet O_2$ in aqueous medium to $^\bullet O_2^-$ by acting as electron donors. A fraction of $^\bullet O_2^-$ contributed directly to the degradation of estrogens, while the other fraction converted to H_2O_2 by reacting with water. Therefore, with the aid of PFRs, the H_2O_2 in the medium led to the formation of $^\bullet OH$ which ultimately ended up degrading the estrogens. The high surface area, oxygen-containing functional groups, and iron hydroxides of the BC contributed to adsorption as well. Furthermore, the authors have observed an increase in E2 removal with increasing pH which is ascribed to the increased PFR content. As the pH increased, the degree of deprotonation of the BC surface increased as well, resulting in an increased rate of reaction due to the favored electron transfer to PFRs. However, in the absence of H_2O_2, the variation with pH was insignificant and is reported to be due to the competitive effect caused by OH^- (Yu et al., 2019).

In another study, Zhu et al. proposed a photocatalytic approach for the removal of E1 by irradiating a Bi/Bi_2O_3 BC composite with UV. The rice husk BC impregnated with Bi/Bi_2O_3 forms PFRs which transfer electrons to form free radicals. The $^\bullet OH$ radicals formed due to the PFRs in the presence of UV irradiation are the main species that contribute to the estrone degradation. Photocatalytic activity is enhanced by the porous structure of the BC composite, enhancing charge separation. When compared to the previous method, the optimum operational pH used was neutral. However, the authors suggest that a slightly acidic medium is more favorable. At low pH values, E1 exists in its molecular form which facilitates its adsorption onto the positively charged BC composite surface and promoting catalytic degradation of E1(Zhu et al., 2020). Thus, catalytic activity of the BC is dependent on the amount and the type of PFRs present on the BC and environmental conditions.

3.10. Microbial influence on the removal of estrogens

Combining microbes with BC facilitates the maximum degradability of estrogens in aquatic environments instead of utilizing BC alone. Microbes, such as bacteria and fungi, carry out various mechanisms to degrade estrogen in the presence of BC. Bacterial activity primarily depends on the high specific surface area of the BC and its composition of functional groups, whereas fungi mainly depend on habituating the BC (Dai et al., 2019; Loffredo et al., 2014, 2016).

The redox-activity and nature of the surface functional groups on BC, such as quinone-semiquinone/hydroquinone, etc., revealed that BC could conveniently accept electrons generated during microbial cell growth and extracellular respiration. As BC can efficiently recover the electrons released by microbial oxidation and nitrogen reduction mechanisms, BC promotes the metabolic processes of cells and enables the degradation of E2.

In one study, Dai et al. evaluated the effect of pyrolysis temperature and concentration of BC used on E2 degradation. At 500 °C, the electron-accepting capacity of some bacteria reportedly increased (i.e. *Shewanella oneidensis* MR-1) and promoted the growth and metabolism of strains that accelerated E2 degradation. Moreover, it was discovered that the concentration of BC influenced the microbial degradation of E2. It was observed that microbial degradation increased significantly when the concentration of BC was increased from 0 to 100 mg L^{-1}. The maximum

degradation efficiency of E2 was observed upon the addition of 50 mg L^{-1} of BC, which increased the degradation efficiency of E2 almost by 2.2-fold as compared to a system that had no BC. This observation was attributed to the increase of electron-accepting sites in BC. However, when the BC concentration was increased further, bacteria were suggested to be habituating the BC sites.

Therefore, microorganisms will not be available for estrogen degradation in the solution. Furthermore, BC could accelerate direct interspecies electron transfer between bacteria such as *Geobactersulfurreducens* and *Geobacter metallireducens* (Zhang et al., 2018). Additionally, BC could mediate the reaction between microorganisms and Fe (III) minerals via an electron shuttle. Hence, previous studies proved that BC derived from straw and melon could accept, donate or mediate a large number of electrons during the metabolism and growth of a variety of microbial cells Yuan et al., 2018. However, it is unclear at present whether BC could accelerate the removal of E2 under anaerobic microbial degradation conditions.

Another approach for the removal of EDC such as E2 from wastewater employs white-rot fungi combined with BC (Loffredo et al., 2014, 2016). In this study, the BC and the fungus were in direct contact, enabling the continuous removal of contaminants. Therefore, the efficacy of this degradation is enhanced with increasing estrogen hydrophobicity. In a study evaluating the effect of combining the two fungi *Bjerkandera adusta* and *Irpex lacteus* with BC, it was evident that although the degradation of E2 took place in the presence of both types of fungi, the degradation took place faster with *B. adusta*. The degradation can be ascribed to the presence of three main extracellular lignin modifying enzymes namely, lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase. The enzyme LiP is absent in *I. lacteus* which is why it showed slower degradation as compared to *B. adusta* (Yang et al., 2013). It can be inferred that the application of BC might have improved the growth of fungi and the production of ligninolytic enzymes which stimulated growth and production of a more significant and denser mycelium in the aquatic environment.

Overall, it can be seen that these studies might contribute to the development of novel, effective and inexpensive strategies to purify estrogen contaminated waters by improving the bio-chemical pathways of fungi and bacteria. Moreover, special attention can be given for the degradation of estrogens via anaerobic processes.

4. Conclusions and future directions

The literature on BC-based sorptive remediation of steroidal estrogens has been scrutinized. Estrogen exhibits electron donor properties owing to the phenolic group and resonance stabilization. Mechanisms such as EDA and pore-filling are likely to occur between HTBC and estrogens due to the extensive graphitization and porosity of the BC. Moreover, the highly functionalized LTBC and hydrochars facilitate estrogen adsorption via H-bonding. A majority of the adsorption studies were seen to best fit the PSO model, implying that the process was governed by chemisorption. The presence of PFRs impart catalytic properties to BC which enables the degradation of the adsorbate. The bacterial degradation of estrogen is enhanced by the presence of functional groups and redox activity of the BC. Moreover the presence of BC provides a habitat for fungi and facilitates the release of ligninolytic enzymes. The authors have attempted to highlight two major research directions. Two main water bodies prone to estrogen contamination are municipal wastewater systems and manure lagoons. As many studies have discussed the influence of matrix components concerning laboratory simulated water samples, investigating estrogen removal from spiked environmental water samples can be considered a prospective research direction. Moreover, breakthrough studies have to be conducted focusing on commercial applications.

CRediT author statement

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Declaration of competing interest

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

Acknowledgement

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2020.110183.

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