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A review of adsorbents engineered from biological materials developed to remediate estrogen pollution in the environment

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ABSTRACT

Rising concerns over anthropogenic impacts on the environment have increased environmental pollution and water quality research which have demonstrated widespread pollutants characteristics in their low concentrations and few government regulations. Pharmaceuticals are an important subcategory of emerging contaminant pollution which consists of natural and synthetic compounds. Steroids are a notable class of pharmaceutical pollutants due to their high binding affinities and activation of signaling cascades at low concentrations. The impacts of hormonal pollutants necessitate remediation solutions. Adsorption technologies are a favorable method of pollutant removal in research due to the ease of implementation, cost-effectiveness, and potential for environmental friendliness. Biologically derived adsorbent materials offer additional potential benefits of employing properties of biological materials, improving biocompatibility, and valorizing biomass. Hydrogels, biomass, and biochar are some of the most environmentally friendly adsorbents in pollution remediation research and there is a sizable base of publications detailing promising results of these materials. Thus, a review of recent publications of hydrogels, biomass, and biochar applied to adsorb estrogens, the largest class of steroid hormones, will allow their findings to be compared. Estrone (E1), estradiol (E2), estriol (E3), and ethinylestradiol (EE2) were focused on in literature alongside other less-researched hormones including prednisolone, progesterone, hydrocortisone, and dexamethasone. Removal efficiencies of E1, E2, EE2, and E3 by hydrogels ranged from 10 % to 93 %, removal efficiencies of E2 and EE2 with biomasses reached up to 99 % with tree bark, and biochar adsorption peaked in capacity of 233 mg/g of EE2 when synthesized from spent mushroom substrate.

1. Introduction

Advancements in environmental research have increased researchers' awareness of less apparent anthropogenic effects on surrounding ecosystems, including waterborne contaminants. Growth in demand for drinking water has improved technologies to measure contaminants in waterways, which has demonstrated that pollutants are more widespread than previously thought [85,110]. While numerous contaminants are known and regulated in municipal water, several pollutants share the same characteristics of being present in low concentrations, chemically stable, and a lack of government regulation regarding their presence such as antibiotics, steroids, antihypertensives, and anti-inflammatory drugs [22,80,110]. So-called emerging contaminants are an increasingly researched field of pollutants due to consistent studies detecting these compounds in waterways and wastewater treatment plants, and the wide breadth of effects they bear on human health and ecosystems [49,50,86].

Past studies regarding the environmental kinetics of pharmaceutically active compounds have confirmed the presence and bioaccumulation of various compounds in soil and sediments in water near the effluents of industrial activity and wastewater treatment plants [18,63]. Estrogenic compounds have been documented not only in surface water but also in groundwater where conditions are conducive to accumulation [14]. Bioaccumulation studies in fish have demonstrated that organisms readily interact with these compounds, and development of ovarian germ cells, fish height, and fish length are quickly altered as well as increasing bioaccumulation within the fish upon repeated exposure [44]. Estrogen receptors in fish amplify the impacts that estrogenic compounds can induce including altering early development, sexual development, gene expression, and neurobehavioral function [14,79]. Sexual development of amphibians as well as sex reversal in aquatic reptiles have been documented when exposed to estrogenic

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pollutants [14].

One of the most prominent subcategories of emerging contaminants for research attention is pharmaceuticals [74]. Pharmaceuticals are often postulated to pose the highest risk to human health and the environment due to their inherent design of inducing responses on organisms and their wide range of potential physiological effects [24]. Studies reporting pharmaceutically active compounds being measured in natural waterways have raised questions about their pervasiveness [29,86]. Pharmaceuticals have been documented to enter the environment in a few primary pathways including industrial waste, agricultural and husbandry waste, and Wastewater Treatment Plant (WWTP) effluent of which a flow diagram representing the major pathways is depicted in Fig. 1. Reports of pharmaceuticals in the environment across numerous countries have documented hundreds of pharmaceuticals or pharmaceutical derivatives [37]. Hormonally active agents are one of the most prominent subcategories of pharmaceutical pollution, consisting of natural and synthetic compounds largely composed of steroids. Environmentally, these compounds pose strong risks as pollutants due to their toxicity at low concentrations and their high chemical stability [102]. Estrogen is one of the main classes of steroidal sex hormones synthesized by mammals for cell signaling in the reproductive system; estradiol (E2) is the most biologically prominent estrogenic hormone, playing one of the largest signaling roles in female reproductive biology [90]. Synthetic estradiol, chemically known as ethinylestradiol (EE2), is a bioidentical molecule to estradiol developed as a pharmaceutical alternative to E2. It is industrially synthesized and functions the same as estradiol by targeting and activating the same nuclear receptors [90]. E2 and EE2 have been documented as emerging contaminants alongside other estrogens including estrone (E1) and estriol (E3) [23]. Other steroid hormones researched in pollution adsorption to a lesser degree include prednisolone (PN), progesterone (P4), hydrocortisone (HC), and dexamethasone (DM) [6,20,33,101].

Modern municipal wastewater treatment plants (WWTPs) are designed to intake wastewater from urbanized centers and remove carbon, nitrogen, and phosphorus from the water. The cleaned water is then disinfected to governmental standards, and the effluent is ejected into the environment [86,110]. While designs and methods to achieve these objectives vary dramatically across countries, few ECs can effectively be removed by typical WWTPs [110]. Because of the growing awareness of pharmaceuticals entering municipal WWTPs that aren't designed to remove these highly stable synthetic compounds, their presence is being increasingly investigated for their activity in WWTPs and potential solutions to solve their reported environmental contamination [86]. Membrane filtration, coagulation, photolysis, radiation, ultrasonic and UV treatments, oxidation, and adsorption of synthetic estrogen have all received research attention with varying success [26,51,56,86,92]. Adsorption technologies are one of the most favorable methods of pollutant removal due to their relative ease of implementation, cost-effectiveness, and potential for environmental friendliness [11,32]. Extensive studies have been published reporting adsorption of hormones onto various adsorbents, but rarely do these reports comprehensively evaluate the environmental impact of the solutions.

It can be difficult to balance adsorption effectiveness with environmental friendliness as the intensity of synthesis, the base of the adsorbent, chemical modifications made, and the chemicals used in synthesis all impact the environmental friendliness of various solutions. While recent publications comprehensively review other environmentally-friendly biological methods of removing steroidal estrogens in wastewater [60] and have reviewed adsorbents of molecules such as E2 [35], the goal of this review is to focus on materials engineered in an environmentally-friendly manner to selectively adsorb steroidal pharmaceuticals. Bio-based adsorbent materials can solve several of these problems and thus reviewing current bio-based adsorbent materials for hormone adsorption such as hydrogels, biomass, and biochar is important to guide research to focus on solutions that are environmentally conscious and effective. Thus, a review of some promising publications in these fields exploring the adsorption of estrogenic compound

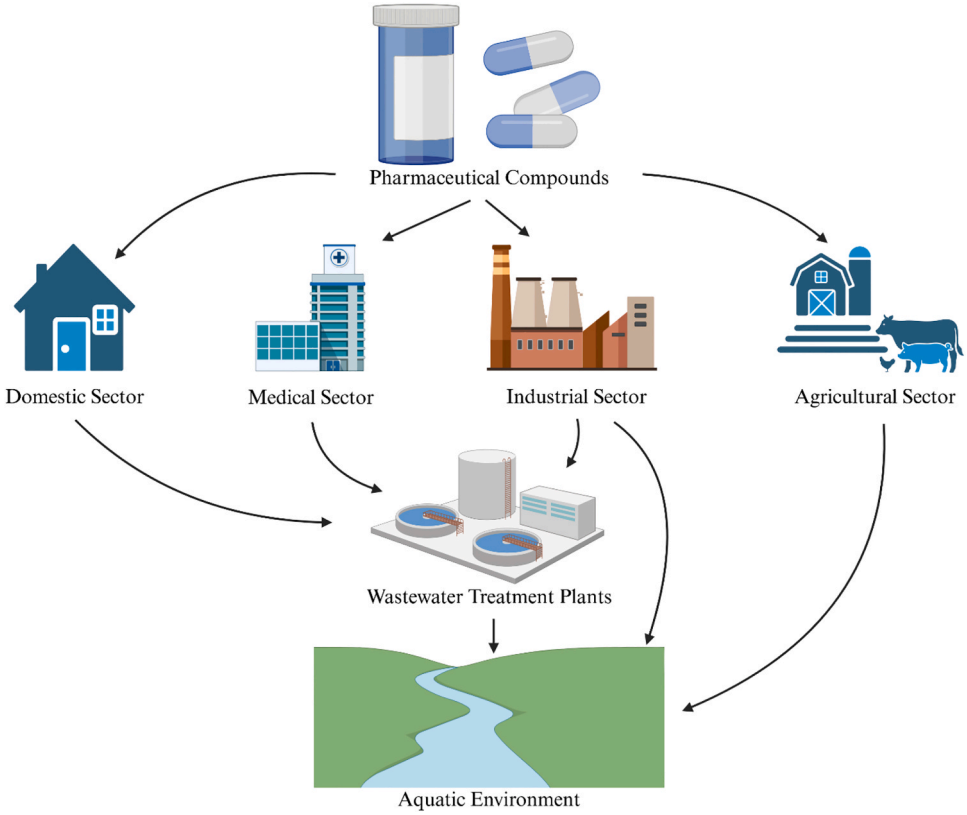


Fig. 1. Common routes of pharmaceutical pollution into the environment. Created in https://BioRender.com.

pollution in water will highlight unique and promising research that will provide a platform for future research to be conducted and to contribute to the growing literature of this topic.

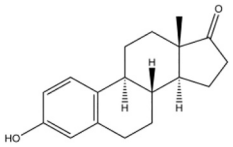
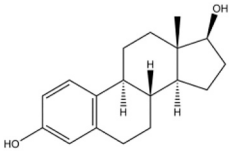
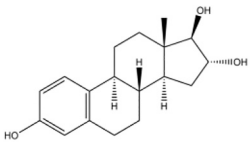
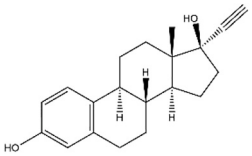
2. Hormone pollution in the environment

Steroid hormones are synthesized endogenously from cholesterol; these water-insoluble molecules readily diffuse through cell and nuclear membranes to reach nuclear receptor proteins [72,90]. Mammalian hormones are characterized by high affinity for their receptors and thus very low cellular concentrations of a hormone are able to trigger large physiological responses. Steroids have a characteristic four fused carbon ring structure which can be modified naturally or synthetically [69], of which several categories of steroid hormones are derived from, the largest of which include estrogens, androgens, and progestogens. Estrogens are often the most impactful pollutants when released into the environment and thus are often most focused on in research [23]. Chemical properties of E1, E2, E3, and EE2 including molecular weight, the octanol water partition coefficient (log K_{ow}), water solubility, and binding affinity for their respective receptors are summarized in Table 1. The octanol water partition coefficient defines the hydrophobicity of a substance; greater than one is hydrophobic and the larger the number above one expresses the degree of hydrophobicity [76].

Anthropogenic activity has been well-documented to be the most prominent source of hormonal pollution, though its different sources can further be divided in addition to other industries including husbandry and industrial activity [24]. Treated wastewater from domestic activity is often listed as the largest source of pharmaceuticals in the environment, and several reports measuring hormonal contamination of effluent confirm this [11,23,63]. Between 2017 and 2020, over 2000 publications testing for pharmaceuticals were aggregated and 40 % of tests for steroid hormones reported positive detection [37]. WWTP effluent was the second-most positive reported category of testing, with 22 % of all positive entries coming from effluent. This rate was only lower than surface water – rivers and streams, which constituted 30 % of all positive entries [37]. Because surface waters such as rivers often receive treated wastewater in addition to runoff from agricultural and husbandry activity, it is likely that this demonstrates the bioaccumulation of pollutants [80]. Just over half of all tests of WWTP effluent reported positive for pharmaceuticals, and just under half of all WWTP effluent tests for pharmaceutical steroid hormones reported positive tests. Most of the positive reports were in liquid, demonstrating pharmaceutical pollution, is much more relevant in waterways and water-based dissemination. Yazdan et al. [110] reported that on average 27 % of ECs are removed by typical WWTPs while a significant percentage are chemically unable to be removed [110]. Because of the growing awareness of ECs and pharmaceuticals entering municipal WWTPs that are not designed to remove these highly stable synthetic compounds, specific micropollutants that are postulated to pose some of the highest risks to human and environmental health are being investigated for their activity in WWTPs, along with potential solutions to solve their reported environmental contamination [86].

Secondary treatment is typically the most impactful step in WWTPs regarding the presence of pharmaceutical compounds. Secondary treatment involves biological digestion of the organic matter in the wastewater by microorganisms, sometimes followed by a tertiary treatment which ensures the water being released is high quality, free of pathogens and other contaminants. Tertiary treatment processes vary the most dramatically from the addition of chemical disinfectants to ozone or UV treatments. Due to the wide variety of pharmaceuticals, the secondary biological processing of pharmaceuticals can range from complete degradation to negative degradation, reversing conjugated metabolites back into the original free compound. Khasawneh & Palaniandy reviewed the effectiveness of several WWTPs worldwide and found removal rates of pharmaceuticals from negative 275 % to over 99 %. In addition to the unique properties of each pharmaceutical, this range can also be explained by the different methods of biological treatments being used. In a review of remediation techniques to solve steroid hormone pollution in wastewater, Bayode et al. aggregated several biological treatment methods of E1, E2, E3, EE2, and BPA and found these biological methods were generally effective at steroid degradation depending on the type of reactor [12]. By contrast, chemical degradation efforts which are often employed in tertiary treatments are typically more binary in their effectiveness against a specific

Table 1
Chemical properties of the three primary natural estrogens (E1, E2, and E3) and the synthetic pharmaceutical EE2.

Hormone	Molecular Weight [71]	Log K_{ow} [71]	Water Solubility [45]	Binding Affinity (pK_i) [104]	Chemical Structure [71]
Estrone (E1)	270.4 g/mol	3.13	0.8 μg/mL at 25 °C	2.357	
Estradiol (E2)	272.4 g/mol	4.01	3.9 μg/mL at 25 °C	2.585	
Estriol (E3)	288.4 g/mol	2.45	3.2 μg/mL at 25 °C	1.854	
Ethinylestradiol (EE2)	296.4 g/mol	3.67	9.7 μg/mL at 25 °C	3.523	

pharmaceutical. One of the most common tertiary treatment methods, the addition of sodium hypochlorite, was found to readily degrade the majority of EE2 in solution but produce products of either similar estrogenic activity or marginally lower [68]. Denitrification treatments were found to heavily degrade natural steroid hormones but have little effect on synthetic hormones [96]. Pure ozone treatment was found to degrade a significant amount of EE2 but not eliminate estrogenic activity in the water due to the metabolites still maintaining high activity [51] whereas combined UV and ozone treatment was found to significantly degrade EE2 in simulated effluent after 30 minutes [92].

Past studies regarding the environmental kinetics of pharmaceutically active compounds have confirmed the presence and bioaccumulation of various compounds in soil and sediments in water near the effluents of industrial activity and wastewater treatment plants [18,63]. Estrogenic compounds including E1, E2, E3, and EE2 have all been documented not only in surface water but also in groundwater where conditions are conducive to accumulation [14]. Studies in fish have demonstrated that organisms readily interact with these compounds, and development of ovarian germ cells, fish height, and fish length are quickly altered as well as increasing bioaccumulation within the fish upon repeated exposure [44]. Estrogen receptors in fish amplify the impacts that estrogenic compounds can induce including altering early development, sexual development, gene expression, and neurobehavioral function [14]. Sexual development of amphibians as well as sex reversal in aquatic reptiles have been documented when exposed to estrogenic pollutants [14].

In studies performed on mice as a human analogue to determine the effects of estrogenic compounds at the transcriptomic level, environmental concentrations of these pollutants were found to significantly alter gene expression in the reproductive system involved in cytoskeleton organization, inflammatory responses, immune responses, and microtubule binding in postnatal mice [78]. It was also suggested that these impacts would be intergenerational and could easily pass from mother to child in mammals. Other studies exposing pregnant mice to estrogenic compounds have found that exposure dramatically alters differentially expressed genes that are associated with latent impact on germ cell differentiation [53]. The past four decades have seen a dramatic increase in human endocrine diseases including tumors and cancers, obesity, hypertension, and heart disease; it is currently hypothesized that increasing exposure to environmental pollutants such as estrogenically active compounds could contribute to these trends [14].

The European Union and the United States constitute the most exhaustive regulations that detail current sources of pharmaceutical pollution [47]. The European Union Commission publishes rolling lists of chemicals that necessitate union-wide monitoring and supervision of which E1, E2, and EE2 were included. This pushed member states to monitor these pollutants and improve the knowledge of the contamination of the environment by these chemicals. Several EDCs have been banned and regulated by various states in the United States, but there is little federal regulation strongly restricting EDC pollution [47]. Because of the worldwide pollution of estrogenic compounds, methods of removal that can not only treat environmental pollution but also remove it from water before it reaches the environment are being increasingly researched. Adsorbents derived from biological materials maintain the benefits of adsorptive materials but also have unique properties that stem from the materials used in synthesis. In addition, biological materials often have the capability of dramatically reducing the environmental footprint of their synthesis when compared to traditional materials. Thus, a review of some of the most promising and well-researched bio-based adsorbents follows to contextualize their capabilities, properties, and environmental impacts.

3. Adsorbents synthesized from biological materials

Adsorption is defined as the attraction of molecules to the surface of a material [81]. In the context of pollution adsorption in water, this method of water treatment is favorable due to the variety of adsorbents that can be used and tuned to adsorb different pollutants. The research field of pollution adsorption is increasingly turning towards biologically derived materials for a few key reasons [20,33]. Biologically derived materials are often more environmentally friendly than traditional materials and ideally can be composted or recycled. In addition, employing residues like biomass that is a generated waste of a separate process that would otherwise be disposed of can add value to these products and further reduce waste, a process termed valorization. Biological materials often have unique chemical properties that can easily be tuned physically or chemically to adsorb a desired pollutant. This can in turn make the production of the adsorbent material cheaper and require fewer intensive processes. Thus, the field of developing bio-based materials to adsorb pollutants has grown dramatically in the past few years with developments that can aid in combating pollution. Some of the largest subfields of bio-based adsorbent materials include hydrogels, biomass, and biochar. These adsorbent materials have been researched regarding their estrogenic adsorption potential, and a summary of most recent publications regarding their testing is shown in Table 2.

3.1. Hydrogels

Hydrogels are a three-dimensional hydrophilic network of chain polymers characterized by their high water capacity, as molecules can diffuse through channels in the matrix and interact with the polymer [36]. Polymers suitable for hydrogel synthesis range widely in properties which can influence the chemistry of the matrix such as the charges on the polymer backbone, the hydrophilicity of the polymer, the crystallinity of the polymer, and the available functional groups. The diversity of applicable polymers has led to a large field of research with a broad range of applications including environmental remediation [77]. Hydrogel chemistry relies on the functional groups and characteristics of the polymers used, which influence chemical interactions within the hydrogel. Thus, the properties of the polymer used are some of the most pertinent facets of hydrogel development to consider. To employ the inherent properties of biological macromolecules, research has focused on synthesizing hydrogels from a variety of polymers derived from natural sources. This method of development improves the biocompatibility and the composting potential of the hydrogels, often facilitates synthesis, can valorize biomass, and often reduces cost [73,75]. Several biopolymers currently receive significant research attention due to these benefits including chitosan, alginate, lignin, zein protein, and pectin. These polymers and their chemical properties are summarized in Table 3. Because hydrogels made from compounds like these can have favorable adsorption of a wide range of compounds, designing them for pollutant removal has been previously demonstrated in various fields with high success [36,100]. Thus, research has turned towards hydrogels synthesized from environmentally friendly and readily available materials for pollutant removal [36].

3.1.1. Chitosan

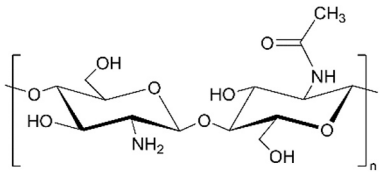
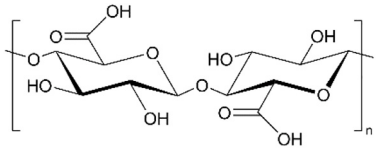
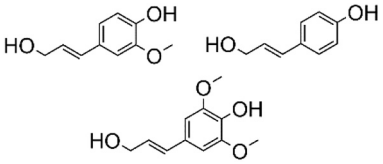
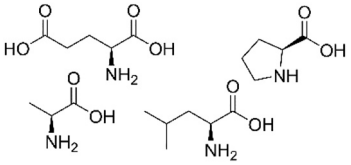
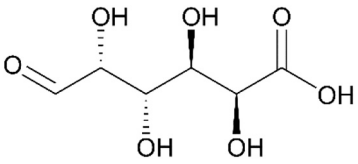
Chitosan is derived from a naturally occurring polymer found in crustaceans with a relatively low environmental impact in its synthesis [70]. Because it is traditionally an industrial byproduct, its applications in new technologies such as hydrogels make it a key example of biomass valorization and the reduction of waste generated [70]. Chitosan consists of two primary monosaccharide units, the deacylated D-glucosamine units, and the acylated N-acetyl-D-glucosamine units, linked in a β-(1−4) configuration [34]. Due to its reactive hydroxyl and amine groups, versatility, and availability, chitosan has become a popular biocompatible polymer used in hydrogel synthesis [66,70]. The versatility of chitosan has grown a large field of research that includes chemical modifications, composite hydrogels, and additives in the matrix to improve performance in their intended applications [34,66,70].

Table 2
Summary of publications of biopolymer-based adsorbents of steroid hormones.

Adsorbent	Steroid(s) Adsorbed	Proposed Adsorption Mechanism(s)	Estrogen Concentration	Adsorption Volume	Adsorption pH	Adsorbent Concentration	Adsorption Time (up to)	Specific Surface Area (m^2/g)	Equilibrium Adsorption (q_e) / Removal Rate (%)	Ref.
Hydrogels										
Alginate-Zein	E1, E2, EE2, E3 & P4	Hydrophobicity	1 mg/L	10 mL	4	N/R	30 min	N/R	N/R	[20]
Pectin-Oak Lignin	E1, E2 & E3	H-Bonds	.01 mg/L	0.5 mL	N/R	10–30 particles	1 hr	N/R	10 % - 60 %	[16]
Chitosan Nanoparticles	EE2	H-Bonds	3.5–11.5 mg/L	200 mL	2 – 12	N/R	10 min – 5 hr	62	2.38 mg/g – 5.86 mg/g	[25]
Alginate-Lignin-Olive Pomace	PN	H-Bonds	4.78–59.75 mg/L	25 mL	5.2 – 6	0.25 g	200 hr	N/R	14.76 % - 48.97 %	[33]
Alginate-Activated Carbon	EE2	Electrostatic	5 mg/L	N/R	3 – 9	5 g/L – 25 g/L	3 hr	N/R	19 % - 93 %	[1]
Biomass										
Rice Husk	E1, E2 & E3	H-Bonds	7–11.3 mg/L	25 mL	7	0.1 g – 0.3 g	4 hr	3.667	52 % - 94.9 %	[32]
Yeast Biomass	E1 & EE2	Electrostatic	1–5 mg/L	5 mL	2 – 10	5 mg – 50 mg	20 min	N/R	28 % - 82 %	[27]
Soybean Hull	E1, E2 & E3	H-Bonds	7–11.3 mg/L	25 mL	7	0.1 g – 0.3 g	4 hr	1.480	81.4 % - 92.6 %	[42]
Microalgae	E1 & E2	Hydrophobicity	1–5 μg/L	1 L	6.8 – 7	0.1 g	6 hr	N/R	9 % - 14 %	[84]
Almond Shells, Coffee Compost & Coconut Fiber	EE2	Hydrophobicity	1 mg/L	160 mL	7	3.75 g	0–20 days	N/R	30 – 36 μg/g	[61]
Pinus elliottii Bark	E2, EE2, P4, HC & DM	Electrostatic	0.5 mg/L	50 mL	5	400 mg	6 hr	N/R	55 % - 99 %	[6]
Cellulose, Collagen & Lignin	E2	Hydrophobicity	10–300 μg/L	10 mL	3.94 – 7.29	0.25 g	24 hr	N/R	0.5 – 10.1 μg/g	[55]
Chitosan & Chitin	E1 & E2	Electrostatic	17.8 – 24.8 μg/L	4 L	3 – 11	2 g/L	140 hr	N/R	0.4 – 0.55 μg/g	[114]
Biochar										
Palm Kernel Shells	EE2	H-Bonds	2 – 8 mg/L	20 mL	3 – 8	50 – 200 mg	3 hr	320	51.8 – 83.1 %	[13]
Corn Straw & Dewatered Sludge	E2	H-Bonds, π-π Stacking	0.5 – 4 mg/L	35 mL	7	5 mg	48 hr	43.6 – 185.3	12.5 – 13.8 mg/g	[39]
Wheat Straw & Cow Manure	E2	Hydrophobicity, π-π Stacking	10–300 μg/L	10 mL	7.43 – 10.2	5 mg	24 hr	2.7 – 383	600 – 2300 μg/g	[55]
Lotus Seedpod	E2	Electrostatic, π-π Stacking	1 – 7 mg/L	50 mL	4 – 10	3 mg	24 hr	25.2 – 364.3	85.75 – 100.6 mg/g	[58]
Rice Straw	E2	π-π Stacking	6 mg/L	50 mL	3 – 12	5 mg	20 hr	31.06	23.09 mg/g	[59]
Wheat Straw & Cow Manure + montmorillonite	E2	π-π Stacking	0.4 – 2.4 mg/L	50 mL	3 – 11	5 mg	24 hr	4.550 – 6.162	5.69 – 11.71 mg/g	[97]
Rice Straw	E2	Electrostatic, π-π Stacking	0.2 – 6 mg/L	50 mL	3 – 12	10 mg	24 hr	Up to 7.66	16 – 22 mg/g	[106]
Walnut Shell	E1, E2 & E3	H-Bonds, π-π Stacking	500 – 2500 μg/L	100 – 150 mL	4 – 11	0.1 – 0.5 mg/mL	12 hr	74.06 – 737.98	1.5 – 2.75 mg/g	[109]
Rice Straw + Attapulgite	E2	H-Bonds, Electrostatic, π-π Stacking	1 – 8 mg/L	100 mL	3 – 11	5 mg	24 hr	11.13 – 203.38	35.21–100.21 mg/g	[111]
Wheat Straw & Peanut Shell	E2	H-Bonds	100 – 4000 μg/L	N/R	N/R	N/R	14 days	8.8 – 19.7	~ 1500 – 1900 μg/g	[115]
Rice Husk	E2	H-Bonds, π-π Stacking	6 mg/L	50 mL	2 – 12	5 – 50 mg	24 hr	1.39 – 119	24.7 – 25.2 mg/g	[113]
Pine Chips	EE2	H-Bonds, π-π Stacking	50 mg/L	100 mL	3.5 – 10.5	200 mg	7 days	972.3 – 1360.3	8 – 10 μM per 200 mg	[46]
Poultry Litter, Wheat Straw, Swine solids	EE2	H-Bonds	100 – 4000 μg/L	8 – 40 mL	7.43 – 10.2	N/R	7 days	2.08 – 8.77	~ 316 – 7900 μg/g	[91]
Litchi + calcium	E1	H-Bonds	1 mg/L	< 50 mL	3 – 13	0 – 200 mg	2 hr	108 – 424	1.12 – 2.09 mg/g	[94]
Mushroom Substrate	EE2 & P4	π-π Stacking	1 – 10 mg/L	35 mL	2 – 12	500 mg	24 hr	246	138.98 – 232.64 mg/g	[101]
Maize straw, Wood dust & Swine manure	EE2	H-Bonds, Pore-filling, Aromatic, π-π Stacking	50 – 3000 μg/L	40 – 60 mL	N/R	N/R	7 days	~ 100 – 550 (CO_2 sorption)	100 – 10000 μg/g	[107]
Pine Chips	E2	π-π Stacking	500 – 1000 μg/L	< 40 mL	3 – 10	0 – 50 mg/L	24 hr	N/R	19.7 μg/L	[48]

* * Prednisolone = PN, Progesterone = P4, Hydrocortisone = HC, Dexamethasone = DM; N/R = not reported

Table 3
Chemical structures of some of the most common polymers used in bio-based hydrogel synthesis. Where the polymers are branched or heterogeneous of several monomers, their most common monomers are shown in lieu of the polymer.

Polymer	Source	Monomer(s)	Functional Group(s)	Chemical Structure/Monomer(s)	Ref.
Chitosan	Chitin, Crusta-ceans	Glucosamine, N-acetyl-glucosamine	-OH, -NH_3, -$COCH_3$		[34]
Alginate	Seaweed	B-D-mannuronic acid, α-L-guluronic acid	-OH, -COO^-		[89]
Lignin	Wood	Guaiacyl, Hydroxyphenyl, Syringyl	-OH, aromatic C_6 rings		[21]
Zein	Corn	Glutamic acid, Leucine, Proline, Alanine	Pyrrolidine, -COOH, -CH_3		[88]
Pectin	Plant cell walls	α−1,4-Galacturonic acid	-OH		[67]

3.1.1.1. Chitosan nanoparticles. Literature exploring the adsorption of estrogenic compounds onto chitosan-based hydrogels is not abundant, but Davarnejad et al. explored adsorption of EE2 onto commercially synthesized chitosan nanoparticles [25]. Chitosan nanoparticles were chosen as it was hypothesized that the hydroxyl groups of the estrogen and the amine groups of the chitosan would participate in hydrogel bonding. This preferential interaction would result in high adsorption efficiency. These nanoparticles were principally raw chitosan and characterization confirmed this. These chitosan nanoparticles were purchased from a private company. Batch adsorption was performed in 200 mL of distilled water with adsorbent quantities ranging from 0.1 g to 2 g and estrogen concentration varying from 3.5 mg/L to 11.5 mg/L. HCl and NaOH were used to adjust the pH of solutions and EE2 concentrations were measured by UV–vis spectroscopy at 280 nm.

Davarnejad et al. first experimented with EE2 adsorption in software-modeled adsorption experiments by varying four dependent variables including pH, time, initial concentration of EE2, and adsorbent dosage [25]. The pH of the solution was not found to play a large role in the adsorption efficiency of the chitosan, which was supported by its point of zero charge, which was found to be roughly a pH of 8. Time of contact also demonstrated minor effects on the adsorption efficiency of EE2 as adsorption of EE2 onto the chitosan occurred primarily within the first hour of modelling. In contrast, initial EE2 concentration and adsorbent dosage played large roles in adsorption efficiency, so the following adsorption experiments were performed at a pH of 7.3, measured to 300 min, had an adsorbent dosage of 1.45 g/L, and had estrogen concentrations varying from 3.5 to 11.5 mg/L. The experimental adsorption equilibrium of estrogen on the chitosan nanoparticles followed a linear positive correlation with the initial concentration of estrogen added. A maximum adsorption equilibrium of 5.86 mg/g was reached with an initial concentration of 11.5 mg/L of EE2. This corresponds to a roughly 74 % adsorption efficiency of EE2 which is favorable, though when the adsorption efficiency of each experiment is calculated, there is an inverse correlation between efficiency and starting concentration. The lowest initial concentration experiment ran at 3.5 mg/L demonstrated the highest efficiency at 98.6 %, though it had the lowest equilibrium capacity of 2.38 mg/g. This relationship likely demonstrates that the polymer is becoming oversaturated with the EE2. Fewer molecules interacting with the chitosan resulted in stronger interactions, but higher concentrations of estrogen did crowd the functional groups of the polymer and could less efficiently adsorb the EE2. In addition, the regeneration potential of the chitosan nanoparticles was explored. 70 % ethanol was used to wash the chitosan, and the regenerated particles were cycled several times to test efficiency with reuse. Adsorption efficiency was maintained over 90 % for 5 cycles and above 75 % over 9 cycles, demonstrating the capacity to reuse these adsorbents several times over.

Davarnejad et al. proposed two primary adsorption mechanisms of EE2 onto the chitosan nanoparticles, both interacting with the amide functional group in the glucosamine monosaccharides. Electrostatic attractions were expected to play the largest role in adsorption between the free hydroxyl groups whereas hydrogen bonding with the free hydroxyl groups may also play a key role.

Chitosan possesses unique chemical properties due to its biocompatibility and reactive functional groups which allow it to contribute to new developing technologies in the medical and environmental sectors.

Because it is produced as a byproduct of the fisheries industry, its newfound applications allows it to further contribute to a circular economy and reduce waste generation. In addition, these properties allow the development of engineered materials that can be tuned to adsorb environmental pollutants such as EE2.

3.1.2. Alginates and corn zein

Alginates are unbranched polysaccharides derived from marine algae with (1→4) β-D-mannuronic acid and α-L-guluronic acid [89]. Alginate polymers are unique in that they bind well and form highly ordered gels with metal ions, often sodium, which makes them ideal polymers for hydrogel applications [7,93]. Alginate is not a biomass produced from an existing industrial process, but its production can be performed in an environmentally friendly manner that can make its application in products such as hydrogels sustainable [8]. By contrast, zein is a water-insoluble heterogeneous polypeptide largely composed of proline, leucine, glutamate, and alanine [88]. Proline, leucine, and alanine are nonpolar amino acids contributing to the hydrophobicity of zein [72]. Because of the chemical properties of zein, it is common to synthesize zein hydrogels composite with polymers such as chitosan or alginate to improve water retention yet benefit from the inclusion of the hydrophobic protein [112].

3.1.2.1. Alginate-zein composite hydrogels. Sodium alginate and sodium alginate-zein hydrogel composite were tested extensively by Castilhos et al. with a wide variety of organic micropollutants including E1, E2, EE2, E3, and P4 [20]. First, the hydrogels were synthesized by adding 4 mL of 2 % weight alginate solution and then 40 μL of 1 mg m/L zein in a 70 % ethanol solution. The mixture was then stirred at 50°C until combined. Adsorption experiments were performed at 10 mL, with 1 mg/L concentrations of contaminants for thirty minutes under stirring. Gas chromatography-mass spectrometry was used to quantify the adsorption of pollutants tested with helium at a flow rate of 1 mL/min, 300 °C and an injection volume of 1 μL. The stability of the hydrogels needed to be considered due to the ion-binding nature of the alginate polymer. The monosaccharides of alginate stabilize themselves by positioning their negatively charged functional groups around positively charged alkaline metals. At neutral pH values, the repulsion between the negatively charged functional groups begin to repel each other which displaces the calcium ions and breaks down the structure of the gel [20,62,89]. Thus, all adsorption experiments were performed in acidic conditions as higher pH values displaced the calcium and collapsed the hydrogel matrix. Hence, when considering the applications of these hydrogels in environmental remediation, their lack of stability at neutral and basic solutions must be accounted for.

E1, E3, and P4 showed large increases in adsorption from the alginate hydrogels to the hydrogel composites, supporting the hypothesis that the zein functional groups more strongly interact with the organic pollutants. Interestingly, EE2 and E2 demonstrated variable changes in adsorption, which both have higher octanol water partition coefficient values. Castilhos et al. [20] concluded that the zein introduces hydrophobicity into the matrix at the expense of water as the hydrogel composites were measured to absorb less water [20]. The combination of alginate and zein produces an adsorbent with both polar and nonpolar regions and thus the water capacity and adsorption of either polar or nonpolar components reflects this. In general, the alginate hydrogels adsorbed polar contaminants more effectively, while the hydrogel composites adsorbed more hydrophobic pollutants. This trend does not account for unique functional groups present in each pollutant and thus some of the measured pollutants that don't follow this correlation could potentially have functional groups that interact with groups in the alginate matrix or in the amino acids. The efficiency of pure alginate hydrogel adsorption was demonstrated for particularly polar compounds, achieving removal efficiency as high as 72 % for paracetamol. In addition to these adsorption tests, one-cycle desorption was also briefly tested which suggested that only a small quantity of the adsorbate was retained and thus reuse would likely be efficient.

Alginate is not a bioresidue of an existing industrial process, but it is easy to produce on an industrial scale and its unique metal ion interactions such as sodium alginate afford it strong and unique adsorption properties as previously mentioned. Its growth, harvesting, and treatment can be done in an environmentally friendly manner that makes its application in products such as hydrogels very sustainable. If developed properly, hydrogels derived from alginate can achieve high adsorption efficiency with a low environmental impact.

3.1.3. Lignin

Lignin is a highly branched structural macromolecule found in plant cell walls [67]. Lacking any repeated or uniform structure, lignin is composed of three primary monolignol precursors consisting of guaiacyl, hydroxyphenyl, and syringyl. Each of these monomers are derived from phenylalanine and thus consist of an aromatic 6-membered carbon ring with a three-carbon chain [89]. Modifications including hydroxyl groups and ethers are added and distinguish various monolignols. Due to its high concentration in aromatic rings and hydrocarbon chains, lignin is hydrophobic and thus can be employed as an effective agent in adsorption of organic compounds. In addition, lignin is an industrial byproduct in which its removal is beneficial for process efficiency as well as biomass valorization [112].

3.1.3.1. Alginate-lignin composite hydrogels. In addition to composite hydrogels, alginate hydrogels can also be modified with agricultural and industrial residues such as olive pomace and lignin. Flores-Céspedes et al. [33] were able to efficiently adsorb PN onto these modified hydrogels and quantify the effect of adding these residues [33]. Both olive pomace and lignin are large biomass byproducts generated by industries which have little use for them, and thus applications such as hydrogel composition are an effort to valorize these residues [33,40]. Both additives were tested in 80 % and 90 % dry weight compositions to determine the effects of the ratio of each additive to the alginate. Aqueous solutions were prepared with 1 or 2 g of sodium alginate and 8 or 9 g of olive pomace or lignin and then stirred vigorously. This mixture was then added to a calcium chloride solution. Adsorption studies with concentrations between 4.78 mg/L to 59.75 mg/L of pollutant for up to 200 hr were performed. The olive pomace hydrogels achieved a much lower equilibrium of approximately 0.3 mg/g versus the lignin hydrogels which achieved an equilibrium of approximately 1.3 mg/g. The variation in concentration of the olive pomace demonstrated little change in the adsorption kinetics as the difference in equilibrium of both 80 % and 90 % olive pomace were statistically insignificant. In contrast, the lignin-composite hydrogels demonstrated much higher adsorption efficiency compared to the olive pomace hydrogels. Up to 25 hr, the adsorption kinetics of the lignin hydrogels exponentially grew and continued to see linear improvements up to 200 hr. There was also a more notable difference in the 80 % and 90 % lignin concentrations as the 90 % lignin hydrogels always measured higher adsorption capacities.

The difference in adsorption of PN between the two residues can be attributed to the chemical composition of lignin and olive pomace. PN is a steroid hormone whose octanol water partition coefficient is 1.62. Thus, the addition of hydrophobic and organic additives including olive pomace and lignin follow work like Castilhos et al. [20] by adding hydrophobic components into a hydrogel synthesized with a well-documented polymer like alginate [20]. The chemical composition of olive pomace however consists primarily of carbohydrates and saturated fatty acids [9] which will interact less strongly with PN than the phenolic rings and hydroxyl groups present in lignin. Flores-Céspedes et al. (2017) also attributed this difference in performance to the higher organic matter content of lignin versus olive pomace and the higher water uptake of the lignin hydrogels [33]. In particular, the more that

water is allowed to permeate the matrix, the more opportunities exist for the PN to diffuse through the matrix and interact with the lignin and bind.

Lignin is another exemplary bioresidue of a production process that otherwise would dispose of the biomass. Extraction of lignin is not environmentally impactful and allows its application to other industries to contribute to a circular economy. Adsorption efficiencies as previously demonstrated with lignin hydrogels can allow production of selective adsorbent materials with minimally impactful materials that are developed from sustainably sourced and processed byproducts.

3.1.4. Pectin

Pectin is a class of polysaccharides characterized by α-(1−4)-linked galacturonic acid that is often heterogenized with other monosaccharides [95]. The most common form of pectin is homogalacturonan which is a linear homopolysaccharide of galacturonic acid decorated with methyl groups at C6 and acetyl groups at O2 or O3 [67]. Variations of pectin exist which can include branched chains of galacturonic acid from the backbone, disaccharides of galacturonic acid and rhamnose, as well as other saccharide substitutions such as xylogalacturonan or apiogalacturonan [67,95]. The variety of functional groups in pectin allow it to be crosslinked into an effective hydrogel matrix that can be tuned to adsorb pollutants, especially when added to a composite hydrogel [16].

3.1.4.1. Pectin-lignin composite hydrogels. Borisenkov et al. [16] experimented with adsorption of E1, E2, and E3 onto pectin-lignin hydrogels in a bio-medical application of adsorbing estrogen *in-vivo* to reduce the risk of breast cancer [16]. Because previous studies demonstrated the possibility that adsorption of hormones and the facilitation of their excretion reduced risks of breast cancer, it was hypothesized that a hydrogel could be developed to serve this purpose. Due to this application, unique considerations were adopted including resistance to degradation in the gastrointestinal environment and low estrogen concentrations in incubation. Pectin hydrogel particles had been previously well documented [57] in drug delivery and thus a pectin-based hydrogel was decided on. A composite hydrogel was synthesized with lignin as it has been shown that lignin binds strongly with estrogens, is resistant to degradation in the gastrointestinal tract, and possesses several functional groups which can interact with pectin to maintain the hydrogel structure [3,16,31,99]. Because lignin composition varies by source, two lignins were tested; wheat lignin, which is higher in hydrocarbon chains, and oak lignin, which is higher in carboxylic and phenolic functional groups. Hydrogels were prepared by first dissolving pectin in an aqueous solution and heating to 40 °C under stirring. One milliliter at a time, the pectin solution was added to an aqueous calcium chloride solution under gentle agitation to form hydrogel beads. Experiments of 10 ng/mL estrogen concentration for one hour were performed with different quantities of hydrogel particles being added. Adsorption efficiency was tested with hydrogels consisting of pectin, pectin and wheat lignin, and pectin and oak lignin. Estrogen concentration quantification was performed by enzyme-linked immunoassay (ELISA).

Adsorption efficiency varied by hydrogel composition. Homogenous pectin hydrogels never attained an adsorption efficiency higher than 20 % with E1, E2, or E3. Both the wheat and oak lignin composite hydrogels adsorbed up to 60 % of estrogens demonstrating the affinity of estrogens for the functional groups in lignin and the success of their interactions. Interestingly, wheat lignin hydrogels adsorbed E1 strongly but not E2 nor E3. Because of this unique selectivity, it is possible that the hydrocarbon chains in the wheat lignin are interacting with the ketone group of E1 which is unique to this estrogen. In contrast, the oak lignin hydrogels adsorbed E1 and E2 up to 50 % - 60 % but below 30 % adsorption efficiency of E3. It is worth mentioning again that these experiments were performed at estrogen concentrations of 10 ng/mL which is low relative to other literature and demonstrate promising results for applications in environmental remediation of estrogens. The lack of adsorption of estrogens to wheat lignin but strong adsorption to oak lignin also mirrors the results of Flores-Céspedes et al. [33] and their additions of olive pomace and pine lignin [33]. Olive pomace was high in saturated fatty acids relative to lignin which was relatively high in phenolic and carboxylic groups. The fatty acid hydrogels in both articles adsorbed less than the phenolic/carboxylic hydrogel demonstrating that pure hydrophobicity is not sufficient to adsorb estrogens, but also functional groups known to interact with estrogens favorably are necessary.

Hydrogels are favorable adsorbents as they can be synthesized from various polymers, can be easily modified chemically or physically, and can be made into composite materials by introducing other products. The freedom to vary the compounds used in creating the matrix allows polymers to be chosen with functional groups, composition, and chemical properties that are most ideal for the intended application of the hydrogel. Due to the hydrophobicity and aromaticity of estrogens, the previously mentioned works often employed composite hydrogels or chemical modifications which maintain the benefits of the hydrogel but while easily improving their adsorption capacity of estrogens. It is likely that given these previous works exploring the adsorption of steroids onto hydrogels, favorable hydrogels for these applications would consist of traditional hydrophilic polymers used for hydrogel synthesis constituting the primary structure of the hydrogel but in a composite matrix with more hydrophobic elements. These can consist of hydrophobic biopolymers like zein or lignin or nonpolar additives. While the field of estrogen adsorption onto hydrogel matrices is not large, existing studies present promising results that can be elaborated and built on for a solution that is cost-effective and environmentally friendly.

3.2. Biomass

Biomass can be defined as plant or animal matter from forestry, agriculture, industrial, or domestic sources which is either the main product of production or a byproduct of an existing process [28]. Existing biomass presents an alternative to developing adsorbent materials that can be more environmentally friendly and less intensive [4,27]. Application of biomass in adsorbent materials can avoid the difficulties of engineered adsorbents that may require intensive and costly production [6]. Developing adsorbents from byproducts of production processes such as tree bark, yeast, rice husk, soybean hull, or microalgae can take advantage of each material's unique characteristics afforded by its chemical structure [6,27,32,42,84]. In addition, valorizing these byproducts of production helps to reduce the environmental impact of the material. Growing literature exists which details the application of these products for the adsorption of environmental estrogen pollution in water. In some cases, these biomasses are physically or chemically treated before testing in estrogen adsorption experiments [6,27,61].

3.2.1. Tree Bark

Because of its wide availability in Brazil, Alves et al. [6] characterized the adsorption of E2, EE2, P4, HC, and DM onto *P. elliottii* tree bark [6]. Tree bark was hypothesized to strongly adsorb organic micropollutants such as these due to the complex microstructure of the wood and the diversity of organic functional groups that could interact with steroids. Surface imaging of the biomass revealed a heterogenous structure of micropores that were deemed conducive to adsorption and energy dispersive X-ray spectroscopy revealed high carbon and oxygen content, reflecting the abundance of lignins and carbohydrates. To test adsorption, 400 mg of adsorbent was added to 50 mL of acidic water spiked with 0.5 mg/L of pollutant. Adsorption kinetics of the tree bark fit the pseudo-second-order kinetic model, Elovich model, and the interparticle diffusion kinetic model, indicating that valence bonding forces with functional groups in the bark were the primary methods of adsorption. In addition, the models supported that the complex internal fibrous structure of the bark allowed high intraparticle diffusion in the

matrix which was expected to contribute to the pollutant removal performance. Removal efficiency of the tree bark ranged from 75 % to 99 % depending on the steroid tested. For all the micropollutants tested except E2, there was a large dependence of temperature found on the adsorption efficiency. For example, DM achieved an equilibrium adsorption capacity of 1.79 μg/g at 15 °C but at 55 °C, this capacity jumped to 2.44 μg/g. The measured change in Gibbs free energy at each temperature decreased with increasing temperature, indicating a higher favorability at higher temperatures. Inversely, E2 adsorption decreasing with higher temperatures was attributed to the two hydroxyl groups on the carbon structure which is unique to estradiol. Because the likelihood of bonding with the hydroxyl groups was much higher in E2, this played a larger factor in adsorption than temperature dependence. While parameters such as temperature and pH dependence can limit adsorption capacity, materials such as tree biomass with complex fibrous networks and a variety of functional groups offer cost-effective solutions that mimic engineered solutions such as hydrogels without needing to synthesize the material.

3.2.2. Rice Husk

Rice husk is a widely produced byproduct of rice production with few applications due to its uniquely high ash content [116]. To valorize this unused biomass, recent literature has explored rice husk to function as a bio-based adsorbent material. Characterization of the material demonstrated high levels of silica and several functional groups including methyl, hydroxyl, and carbonyl groups [32,116]. Thus, their exploration as adsorbent materials have extended to estrogenic compounds where Honorio et al. explored their adsorption capacity of E1, E2, and E3 individually and combined [32]. For monocomponent systems, 0.3 g of biomass was added to 25 mL of solution for E2 and E3, and E2 was tested at 0.1 g in 25 mL. Estrogen concentrations tested were 8, 10.5, and 11.3 mg/L. For combined systems, 0.1 g of rice husk was added to 25 mL of solution containing 7 mg/L of each hormone. Equilibrium adsorption capacity was also evaluated in different solution pH levels ranging from 3 to 12. The effects of solution pH were promising as the point of zero charge of the husk was roughly 7 and thus adsorption efficiency was highest at neutral pH. Individual removal of E1 reached equilibrium at 60 min with a removal of 2.13 mg/g. E2 removal equilibrium was achieved at 120 min with an adsorption capacity of 0.73 mg/g, and E3 removal equilibrium was also achieved at 120 min with a capacity of 0.27 mg/g hormone adsorbed. Respectively, these adsorption capacities demonstrate efficiencies of 86 %, 95 %, and 85 %. In both monocomponent and multicomponent studies, E1 demonstrated the highest affinity for adsorption, then E2 and E3 [32]. All three monocomponent systems were well described by the pseudo-first-order model indicating that the number of active sites on the husk is the primary limiting factor for estrogen adsorption. It was also noted that adsorption kinetics nor capacity did not change for all hormones tested between mono and multicomponent systems, indicating there was no competition between the three steroids.

The rice husk was characterized to be composed primarily of cellulose, lignin, and hemicellulose which are notable for their abundance of hydroxyl groups. Honorio et al. proposed hydrogen bonding to be the most likely adsorption mechanism for each estrogen molecule with their respective functional groups participating in interactions.

3.2.3. Yeast biomass

Another application of a byproduct used for pollutant adsorption was demonstrated by Debs et al. where yeast biomass from the ethanol production industry was tested for its estrogen adsorption performance [27]. The ethanol production process requires yeast for the fermentation of alcohol and thus there is a constant supply of spent yeast biomass produced as a byproduct of the industry [17]. The high carbon content of yeast makes it a promising adsorbent of organic molecules and their application would valorize this byproduct. Thus, the adsorption potential of E1 and EE2 was tested varying the pH, biomass dosage, and hormone concentration. The ranges of variables respectively were pH 2–10, 5 mg to 50 mg, and 0.5 mg/L to 1 mg/L. The quantity of biomass added and the pH of the solution presented the largest positive effect on estrogen adsorption whereas hormone concentration was not statistically significant in its effects on adsorption kinetics. A basic pH of 10 demonstrated a significant increase in adsorption and Debs et al. [27] attributed this to the acidic sites of the yeast including amine, hydroxyl, and thiol functional groups [27]. These groups have pKa values above 8 meaning they are deprotonated at basic pH levels contrary to EE2 which is protonated at high pH values. Thus, it was hypothesized that physical electrostatic interactions were the primary mechanism of estrogen removal and after experimental adsorption data was fit to a Freundlich model, the adsorption was determined to be limited by the capacity of the yeast.

In addition, Debs et al. [27] explored combined E1 and EE2 adsorption to determine if competition existed in adsorption onto the yeast biomass. In contrast with Honorio et el. (2020), moderate competition was demonstrated between E1 and EE2, particularly when the concentrations of each hormone was varied [32]. Whereas Honorio et al. (2020) exhibited no change in the kinetics of adsorption between mono and multicomponent systems, Debs et al. [27] found when E1 concentrations were raised, EE2 adsorption dropped and vice versa [27, 32]. This could be mirroring results from Borisenkov et al. [16] where they found wheat lignin hydrogels selectively adsorbed E1 over E2 or E3 [16]. This could again be attributed to the ketone group on E1 which no other estrogens here possess. In addition, this could be further impacted by the pH of the solution as Debs et al. [27] experimented at pH 10 which deprotonated the majority of the yeast functional groups whereas Honorio et al. experimented at a neutral pH on rice husk [27,32].

3.2.4. Soybean Hulls

Soybean hulls are the largest byproduct of the soybean production process with little application due to their minimal nutritional content [54]. Soybean hulls primarily consist of cellulose, hemicellulose, lignin, protein, and mineral salts which contain various functional groups including hydroxyl, carboxyl, and methoxy groups [42]. In addition, physical analysis of hulls reveals porous and fibrous networks which naturally favors adsorption of molecules [42]. Thus, research regarding their application as adsorbent materials has been explored in the past for pollutants such as heavy metals [54,64,82] and dyes [10,41,65,83]. More recently, Honorio et al. [42] investigated their potential as adsorbents of estrogen pollution from husbandry activity [42]. Adsorption experiments were run with E1, E2, and E3 in concentrations ranging from 2 to 13 mg/L and pH values from 4 to 10. The pH was found to have a large effect on the adsorption due to the charges of the estrogens. As the hormone becomes more charged with acidic and basic solutions, the solubility of the steroid increases which reduces its affinity for the adsorbent which benefits from hydrophobic interactions for adsorption. Thus, neutral pH values demonstrated the most optimal adsorption capacities where interactions were primarily π-π stacking, hydrogen bonding, hydrophobicity, and steric interactions. All three estrogens were found to reach equilibrium within two hours and removal was found to be over 90 % for E1, E2, and E3. Morphological studies found the soybean hull was primarily found to be mesoporous with some micropores which was demonstrated with the higher removal rates of the smaller E1 molecule.

3.2.5. Discussion

Other research articles have been published regarding estrogen adsorption onto biomass with varying success. Ruksrithong & Phattarapattamawong [84] explored the adsorption of E1 and E2 onto two different strains of microalgae and found approximately 10 % removal of aqueous estrogen [84]. In this instance, estrogen degradation by the algae was found to be much more effective due to primarily negative surface charge of the algae [84,98]. Loffredo et al. [61] tested the adsorption of EE2 from municipal landfill leachate with almond shells,

coffee compost, and coconut fiber to great removal efficiency but only after 20 days of incubation [61]. Li et al. [55] tested raw collagen, cellulose, and lignin polymers for their adsorption capacity of E2 [55]. Each macromolecule demonstrated linear isotherms which indicates adsorption onto the polymer surface. Lignin adsorption performance was found to be significantly more efficient than collagen or cellulose, likely due to its high aromaticity and hydrophobicity which allows strong π-π stacking, hydrogen bonding, and hydrophobic interactions with the estrogen. These results mirror Borisenkov et al. [16] where the estrogen adsorption capacity of pectin hydrogels was improved significantly with lignin added to the matrix [16]. Thus, interactions including π-π stacking and hydrophobic interactions are likely some of the most optimal methods of adsorbing these aromatic organic micropollutants.

Previous adsorption experiments of biomass demonstrate the necessity of either a complex polymer network, available functional groups that are reactive with estrogens, hydrophobicity, or some combination of these characteristics. Biomass such as lignin is a promising material for estrogen adsorption due to the aromaticity and hydrophobicity of the chemical structure of lignin. By extension, materials such as tree bark and soybean hulls increase the adsorption potential due to their complex fibrous network and introduction of other compatible functional groups for bonding, respectively. These materials present an environmentally friendly and cost-effective method of estrogen removal from the environment.

3.3. Biochar

Pyrolysis is the process by which biomass is heated in an oxygen-limited atmosphere to achieve thermal degradation [108]. The resulting products are gases, liquid oil, and the carbon solids left by the biomass [28], which is termed biochar [5]. Biochar is unique in properties due to its fixed carbon content, variety of functional groups, high specific surface area, physiochemical stability, and high porosity [13,39,108]. In addition, its ability to be synthesized from byproduct biomass contributes to its environmental friendliness and can valorize otherwise waste biomass [48,59]. Thus, research in the past decade has been directed towards its development and applications in various fields including agriculture, medical applications, and environmental remediation [59,108].

3.3.1. Biochar preparation

Operating conditions of pyrolysis have large effects on the biochar produced [46]. Parameters including residence time, temperature, biomass used, and atmosphere of degradation all impact the biochar reaction process [28]. Thus, operating parameters can be divided into four primary categories of which torrefaction and conventional pyrolysis are the most common, at temperatures below 300 °C and 550–950 °C, respectively [28,108]. Torrefaction can significantly preserve the functional groups of the biochar and improve mechanical properties as low temperatures retain aliphatic and cellulose structures due to the lack of complete carbonization [13,107,108]. Conventional pyrolysis allows slow and complete degradation of the solid biomass into a complete and uniform carbonized solid product and includes chemical modifications including carbohydrate decomposition, decarboxylation, and decarbonylation [87]. Conventional pyrolysis facilitates the formation of aromatic carbon structures and complex pore structures [107] which can facilitate adsorption kinetics.

3.3.1.1. Biochar feedstocks. Because each biomass is composed of different organic compounds and ratios between each compound, the thermal degradation of each stock will vary in its residence time, stability, and final products [108]. This variation necessitates researchers to experiment with different feedstocks and processing parameters but allow tuning of the final product to be optimized for the intended application of the biochar [115]. Several research articles have been published exploring the adsorption of environmental estrogen pollution into biochar as it is naturally hydrophobic, can be environmentally friendly, and often cost-effective to produce. Different pyrolysis parameters, post-synthesis treatment methods, composites, and different biomass feedstocks have all been explored previously to varying degrees of success. It is therefore valuable to review some of the most impactful research articles to evaluate recent progress and direct future research towards the most promising adsorbents.

3.3.2. Conventional pyrolysis

Li et al. [55] researched the E2 adsorption capacity of biochar in the context of soil pollution of estrogens and understanding the kinetics of E2 in soil [55]. Biochar was synthesized from wheat straw and cow manure to test the different chemical compositions of the organic matter, and three different pyrolysis temperatures, 350 ºC, 550 ºC, and 700 ºC were experimented with. Adsorption experiments were performed in calcium chloride and humic acid; 250 mg of biomacromolecules were added with 5 mg biochar into a 10 mL solution of E2 where concentrations were ranged from 10 μg/L to 300 μg/L. After 24 hours of shaking incubation, adsorption experiments demonstrated that higher pyrolysis temperatures were much more effective at adsorbing E2. Both 700 ºC biochar samples demonstrated over 2000 μg/g adsorption performance whereas neither sample synthesized at 350 ºC adsorbed over 1000 μg/g. The wheat straw biochar also demonstrated much higher adsorption performance of the estrogen, particularly at lower temperatures. It is demonstrated here that the higher temperatures induce higher hydrophobicity and concentrations of aromatic groups, both of which interact more extensively with the estrogen through π-π stacking thus increasing the adsorption capacity of the biochar dramatically [55].

3.3.2.1. Agricultural waste. Agricultural waste can be a great biomass source for biochar production as they are often very economical and are produced regardless of their applications. Spent mushroom substrate is suitable for this application as mushrooms grown can generate around five times their mass in substrate [52]. Vieira et al. [101] experimented producing biochar from mushroom substrate at different temperatures and residence times ranging from 250 ºC-600 ºC and 10 min to 60 min, respectively [101]. 600 ºC was found to have the highest adsorption capacity and thus was more thoroughly tested. EE2 and P4 were tested at 1 mg/L and 10 mg/L respectively at 35 mL for 24 hr at room temperature. Removal efficiency of EE2 and P4 was measured 89 % and 91 % respectively and reduced slightly with longer time measurements. This quick adsorption measured is hypothesized to be due to chemical bonding with the hormones and functional groups on the surface of the biochar. FT-IR analysis revealed bands at 1699 cm^{-1} and 1632 cm^{-1} which was indicated as C═O and C═C groups which were proposed to interact their π electrons with the steroid molecules. It is worth noting EE2 took approximately 10 minutes to reach equilibrium adsorption whereas P4 required 45 min to reach equilibrium adsorption. This could support the hypothesis that π-π stacking is the primary adsorption mechanism as P4 lacks the aromatic 6-membered carbon ring that EE2 has. The adsorption kinetics of EE2 and P4 demonstrated by biochar synthesized from spent mushroom substrate are very promising as they are efficient in a reasonable period. The application of agricultural waste further improves the cost effectiveness and environmental compatibility of this method of hormone remediation.

3.3.2.2. Effects of temperatures in conventional pyrolysis. As mentioned previously, biochar chemistry can be complex due to the feedstock and process parameters of synthesis such as the temperature of pyrolysis. Wang et al. [107] sought to understand the chemical effects of varying biomass and temperature in biochar production and thus their effects on EE2 adsorption [107]. Three different biomasses were chosen to be experimented with at a range of temperatures; maize straw, pine wood dust, and swine manure were tested in biochar production at

temperatures ranging from 250 ℃ to 600 ℃. All biochar samples analyzed found a reduction in polar functional groups and an increase in hydrophobicity with higher thermal treatments. NMR spectra revealed that oxygen-containing functional groups generally decreased with increasing treatment temperature, which is likely related to the reduction in polar groups. Manure biochar was found to be less polar than the straw or wood biochar, likely due to the high mineral content in the feedstock, as mentioned by Wang et al. [107]. In addition, increasing temperatures correlated strongly with aromatic functional groups and inversely with aliphatic carbon content. Higher temperature biochars generally adsorbed EE2 more efficiently than lower temperature biochars, but the authors attribute two different adsorption mechanisms depending on how high thermal treatment was performed at. Due to the high concentration of polar groups in biochars treated at lower temperatures, hydrogen bonding with the hydroxyl groups of the EE2 is likely the primary adsorption mechanism. However, at higher treatment temperatures, these polar functional groups are lost and replaced with hydrophobic and aromatic functional groups. Hydrophobic interactions and π-π stacking are likely the dominant chemical interactions with high-temperature biochars which may be more effective than hydrogen bonding as Wang et al. [107] often found higher temperature biochars to demonstrate better adsorption of EE2 [107]. Because higher temperature also facilitates larger and more complex pore structures, it is likely that pore-filling also contributes to the improved adsorption capacity of high temperature pyrolyzed biochars.

3.3.3. Torrefaction

Because of the benefits of torrefaction, Beri et al. [13] experimented with biochar production from palm kernel shells at lower pyrolysis temperatures for the adsorption of EE2 [13]. Hydrothermal carbonization of the kernels was carried out at 200 ℃ in order to preserve the functional groups of the biomass and steam activation was performed at 500 ℃ to increase the specific surface area of the shells. Adsorption experiments were performed between pH values of 3–8, estrogen 2 – 8 mg/L, and biochar mass from 50 – 200 mg in 20 mL of estrogen solution. Adsorption efficiency was found to range between 50 % and 90 % with the largest effects coming from the pH of the solution where estrogen adsorption was most efficient at lower pH values. The point of zero charge of the biochar was found to be 5.13 and the acid dissociation constant of EE2 is 10.4, and thus at lower pH values the biochar is positively charged whereas the estrogen is more negatively charged. Interestingly, the addition of more biochar minimally impacted the adsorption performance though the authors attribute this to the agglomeration of particles which reduced the exposed surface area. While the adsorption capacity of the biochar could be improved regarding more real-world conditions, hydrothermal carbonization was demonstrated to be an efficient method of producing biochar designed for the adsorption of estrogens.

3.3.4. Discussion

The unique properties of biochar make its capacity for estrogen adsorption very favorable which has led to a wide variety of feedstocks and synthesis protocols being explored, as demonstrated by the previously highlighted works. Corn, wheat, and rice straw, dewatered sludge, shells and seedpods, wood trimmings, manure, and bedding have all been explored often with good efficiency due to the biomass feedstocks [13,30,39,48,55,58,59,91,97,107,109,111,115]. As also demonstrated by Abdel-Gawad & Abdel-Aziz [1], carbon adsorbents such as these can be added to hydrogel matrices to form composite adsorbents that can benefit from both technologies [1]. The chemical properties of estrogens including their hydrophobicity, aromaticity, and polar functional groups allow them to be adsorbed through various mechanisms that biochar can be designed to take full advantage of in a cost-effective and environmentally friendly manor.

4. Environmental Analysis of Adsorption Technologies

Environmental impacts of products are often evaluated by Life Cycle Assessments (LCA), which is an internationally standardized set of analyses (ISO 14040:2006) used to determine a variety of environmental impacts of a desired system [19]. LCAs notably include environmental impacts of most or all processes that contribute to a system including manufacturing, transportation, maintenance, operation, construction, and decommissioning [15]. LCAs can help to inform decision making about a product or process and identify areas of a process that can be improved (Environmental Management - Life Cycle Assessment - Principles and Framework, 2006). Standardized LCAs are most useful in that their environmental impact results including global warming potential, ozone depletion potential, photochemical ozone creation potential, and abiotic depletion are reported in standardized units and thus can be relatively compared to other assessments performed in similar conditions. LCAs of water treatment technologies are relatively uncommon in published literature but are plentiful enough to make meaningful comparisons.

Comparisons of LCAs must be made carefully as some of the most impactful aspects of adsorption technologies such as source material and energy production vary dramatically by location and thus must be considered. Assessing the environmental impact of location for a particular adsorbent material is difficult to compare [5]. The distances a product must travel to its final destination for material synthesis varies dramatically between location of the researchers, location of the adsorption, and source of the material. The method of electricity generation also varies dramatically and thus can contribute heavily or very little depending on if the energy was generated from fossil fuels or from renewable sources, respectively.

While some comparisons can be drawn between life cycle analyses performed between adsorbent materials in regards to removal of pollutants, it isn't feasible to quantify and compare the environmental impact of a given pollutant being left in the environment versus the environmental impact of a pollutant being removed with an adsorbent including the environmental impacts of its production, usage, and disposal. To provide a reference for the environmental impacts of various adsorption technologies, they can roughly be compared to the impacts of wastewater treatment processes, particularly the tertiary polishing treatments which are often the most comparable to technologies being developed for pollutant removal such as filters, membranes, and adsorbent materials. Thus, some of the primary biologically based adsorbent materials developed for pollutant adsorption including hydrogels of various bases, biochar, and activated carbon can be assessed for their environmental impact and compared to the impacts of conventional wastewater tertiary treatment.

4.1. Polyvinylidene fluoride

In order to contextualize the environmental impact of a given bio-based adsorbent material developed for water treatment, it is useful to review LCAs of current water filtration technologies which are often petrochemical-derived polymers. Polyvinylidene fluoride is a common polymer used in wastewater treatment plant filters and thus makes a suitable comparison [43]. While bio-based adsorbents are often intended to be used as an additional step in filtration for pollutants found in wastewater, comparisons can help draw some meaningful conclusions. Hu et al. [43] performed a comprehensive life cycle analysis of the resource extraction and production of a functional unit of 1 kg of PVDF water filter. Because there are two primary routes of synthesis of PVDF, both were analyzed by LCA. Both routes provided similar results being 54.7 kg CO2 and 55.8 kg CO2 global warming potential, which were compared to similar analyses previously reported in literature which were agreeable. The primary contributions to the GWP of PVDF were the energy consumed in the production process and the environmental impacts of the chemicals used in synthesis, though it should be noted

energy production was calculated to be provided by coal and thus may be less when used with natural gas or renewable resource-generated energy. PVDF synthesis was calculated to contribute most heavily to terrestrial ecotoxicity, climate change, human non-carcinogenic toxicity, and fossil resource scarcity [43].

4.2. Hydrogels

Environmental analyses of many hydrogels do not exist in literature, but Gujjala & Won [38] performed an extensive economic and environmental analysis of lignin-based hydrogels designed to adsorb heavy metals in the environment [38]. LCA analysis was performed on one kilogram of lignin-based hydrogel production, though factors including use and disposal were not considered. Per kilogram produced, climate change simulation calculated the emission of 2.8 kg CO2 eq. and fossil fuel depletion was 1.1 kg Oil eq. It was found that the majority of contributions to these impacts was production of the hydrogel itself and the majority of the production impacts came from the chemicals being used in synthesis (60–70 %). Acrylic acid synthesis in particular contributed heavily to categories including climate change due to its synthesis pathway including the oxidation of fossil fuel-based propylene. The second highest contributor to the environmental impacts of the hydrogel was found to be heat and power generation which came primarily from natural gas.

Wang et al. [105] developed modified chitosan composite hydrogels for the adsorption of environmental phosphorus pollution primarily deriving from eutrophication, each a combination of lanthanum and calcium [105]. Similar to Gujjala & Won [38], production of the hydrogels was analyzed by LCA but the usage and disposal of the hydrogel was not considered. In addition, waste liquid generated was not considered and synthesis conditions between each hydrogel was considered identical. Per kilogram of hydrogel synthesized, the lanthanum hydrogel was calculated to emit the most carbon dioxide in production, being 26.3 kg CO2. Lanthanum-calcium composite hydrogels emitted the second most atmospheric carbon dioxide at 24.73 kg CO2. The lanthanum chloride was calculated to emit the majority of carbon dioxide, approximately 60 % for both hydrogels whereas the chitosan was the second largest carbon producer at approximately 23 %. The chitosan hydrogel and calcium-chitosan hydrogels generated similar carbon dioxide at 13.8 kg CO2 and 12.8 kg CO2, respectively. Chitosan was by far the largest carbon dioxide emitter in these hydrogels, producing approximately 70 % of the atmospheric carbon dioxide. Lanthanum was found to affect a wide variety of environmental parameters including marine eutrophication, terrestrial, freshwater, and marine ecotoxicity, human carcinogenic toxicity, land use, and mineral resource scarcity. Chitosan was found to most dramatically impact water consumption [105].

In addition to the comparisons that can be drawn between each of the four hydrogels synthesized by Wang et al. [105], it is interesting to note the results published of the global warming potential are normalized to phosphorus adsorbed, not by kilogram of hydrogel synthesized. When normalizing for hydrogel adsorption efficiency, the Lanthanum-calcium composite hydrogel becomes the least impactful emitter at 24.73 kg CO2. The most impactful emitter becomes the chitosan hydrogel at 57.92 kg CO2, and the calcium and lanthanum hydrogels fall in the middle at 46.25 kg CO2 and 33.96 kg CO2, respectively. This reversal in environmental impact demonstrates another facet to consider when analyzing the environmental impact of adsorbent materials for the application of pollutant adsorption which is the performance of the adsorbent material. High performing materials with synthesis protocols that emit large quantities of atmospheric carbon dioxide may be more environmentally sustainable when compared to a much less intensive material to synthesize that has much lower adsorption efficiency.

4.3. Biochar and activated carbon

Carbon-based adsorbent materials have been researched for quite a few years in their capacity to adsorb pollutants in water and thus literature regarding their application is much more through, particularly LCAs regarding their application and efficiency. Both activated carbon and biochar have had extensive studies published regarding their adsorption performance and environmental impacts, and thus meta-analyses comparing several papers have been published. Alhashimi & Aktas aggregated the LCAs of over eighty types of biochar and activated carbon published regarding their adsorption capacity of heavy metal pollution [5]. Global warming potential of activated carbon and biochar of various sources was aggregated and found to show a stark difference; due to the inherent carbon sequestration in the production of biochar, the emitted carbon dioxide was almost always calculated to be negative. Most sources of biomass for biochar production resulted in carbon dioxide emissions between −1 and 0 kg CO2 emitted whereas activated carbon synthesis was found to range from 1.2 kg CO2 to 11 kg CO2 emitted, depending on the source. Energy demand was found to follow similar patterns where consumption for biochar averaged 1–2 MJ/kg where activated carbon ranged from 44 to 170 MJ/kg. Environmental impact per unit of pollutant removed as opposed to per unit of adsorbent synthesized was also analyzed and similar results were found, due to the often higher adsorption capacity of biochar over activated carbon. While the confidence intervals were wide, activated carbons were found to consistently emit more atmospheric carbon dioxide per unit of pollutant adsorbed when compared to the biochar. The authors concluded the article discussing that even though biochar has more desirable capabilities in nearly every aspect quantified, it is much less frequently used than activated carbon in applications such as water filtration and adsorption. Some barriers proposed included less consistency in biochar adsorption and performance as well as the activation time of biochar [5].

Activated carbon is widely employed in water filtration but its synthesis and source material can vary widely and thus the corresponding environmental impacts are subject to large fluctuations. Vilén et al. performed comparative life cycle assessments of activated carbon produced from virgin coal, reactivated coal, and three bio-residues including peat, coconut, and wood [103]. Wood and peat were included to represent locally sourced bio-residues and these were compared against a globally sourced bio-residue of coconut shells and traditional fossil-fuel based sources like coal. LCA methodology was used according to ISO standards, use and end-of-life stages were omitted, and calculations were done on a 1 kg of activated carbon unit basis. Virgin coal-based activated carbon was calculated to have the highest environmental impact in nearly all impacts examined. The categories in which coal based activated carbon was over twice as much as impactful as the second largest contributor was seven of the twelve categories. Global warming potential of coconut, wood and reactivated coal carbon were found to be the lowest at 1.1 kg CO2, 0.9 kg CO2, and 2.1 kg CO2. Peat and virgin coal based activated carbon were found to be the highest contributors at 6.7 kg CO2 and 9.5 kg CO2, respectively. Overall, the production of the activated carbon was found to have the largest environmental impacts and transportation was found to have very little impact on the environment [103].

4.4. Discussion

Life cycle analyses are invaluable tools for analyzing the environmental impact of a given process or product, but it must be stressed that due to the variation of a given process including transportation of materials, methods of electricity and energy generation, input product sources, and usage of products all vary dramatically and make direct comparisons of LCAs difficult. Regarding adsorbent materials for the purpose of pollutant removal, these variations are even larger due to the lack of LCAs published regarding these materials, the variation in

desorption and readsorption between different materials, the desired use of a developed material, the lifespan of a given adsorbent, contextualizing the results of a given LCA, the necessarily small system boundaries analyzed, and where the materials were developed. When these limitations in LCAs are properly understood, meaningful comparisons can be made regarding analyses performed between different adsorbent materials.

Most prominently demonstrated in the PVDF and hydrogel analyses was that the primary contributors to global warming potential were often the input chemicals used in synthesis. Both synthesis pathways of the PVDF require strong chemicals that either require intensive energy to produce or are well known ecotoxic chemicals such as TFE and R-132b, respectively. In the hydrogel analyses, acrylic acid and lanthanum ions were both calculated to be large contributors to global warming potential which largely overshadowed other contributors such as energy consumption. These results demonstrate that chemicals used in synthesis can contribute heavily to the environmental impact of a given product and thus careful consideration must be taken when choosing chemicals for the synthesis of a product.

Comparing the life cycle analysis of biochar and activated carbon produced interesting results as the environmental impact of biochar was often negative while the activated carbon was minimal to moderate. As mentioned previously, this results from the ability of biochar to sequester carbon and makes biochar even more appealing compared to activated carbon when its adsorption efficiency can exceed traditional carbon. As mentioned by Alhashimi et al. [117], it is necessary to address the differences between the end-of-life of biochar and activated carbon as biochar isn't easily desorbed yet activated carbon can be desorbed relatively easily. The comparison between the necessary new synthesis of biochar with the energy demand of re-activating carbon was simulated, and it was found that the energy required for re-synthesis of biochar never exceeded the energy required for re-activation of carbon.

While desorption of hydrogels is a relatively under-addressed topic and varies widely based on the hydrogel being used, common desorption strategies include acids, bases, and solvents which are chemicals that can either be synthesized in a way that is environmentally friendly or there are alternatives that are environmentally compatible [2]. Because of the desorption potential, hydrogels may be among the least impactful adsorption methodologies due to the ability to synthesize environmentally friendly hydrogels and use desorption solvents are not intensive to produce.

When comparing the PVDF filter synthesis analysis to all other LCAs analyzed including various hydrogels, biochar, and activated carbon, its global warming potential was calculated as almost double the second largest contributor of lanthanum hydrogels. These analyses demonstrate how intensive it is to synthesize plastic based water filtration membranes and how much room for improvement there is in the field of reducing the environmental impact of these filters.

As some of these papers mentioned during their LCAs of different adsorbent materials, a typical LCA would be performed per unit of synthesized product, most often one kilogram. While performing LCAs of adsorbent materials, comparison between analyses and better comprehension of the performance of the material itself would be improved if the functional unit was the mass of adsorbate captured by the material. This would improve analysis by two factors as this would include the efficiency of the material for adsorption, which is otherwise omitted from the LCA calculation, and if a material requires intensive synthesis but is highly efficient to the point the efficiency offsets the synthesis, this would also be included in the calculation. These changes push the primary goals of LCAs forward, to quantify environmental impacts of a process at each step and allow designers to identify opportunities to improve environmental compatibility of a process.

5. Adsorbent comparisons

Worldwide pollution of pharmaceuticals is increasingly being documented and requires immediate action to curb its impact on the environment, ecosystems, and human health. Adsorption of these pollutants is a favorable solution due to its flexibility and ease of implementation. Because adsorbents can be synthesized in various forms from a wide range of materials, they can be optimized for cost-effectiveness, environmental compatibility, adsorption capacity, or ease of synthesis. Bio-based adsorbent materials can meet all these parameters as biological material can be easily sourced, can be inexpensive, and have unique chemical properties that often can be easily modified. A flowchart of the discussed adsorbent materials is depicted in Fig. 2.

However, these bio-based adsorbents are not currently in large-scale application for environmental remediation for various reasons. By directing future research to solve these limitations, their implementation into bioremediation projects could become possible. Thus, Table 4 highlights some common aspects of adsorption and novel results previously discussed which can be focused on incorporating in future research. Choosing the optimal adsorbent materials and the desired methods of adsorption can be key in developing successful solutions to remediate environmental pollution.

Hydrogels are some of the most flexible adsorbents for application due to the abilities of researchers to choose polymers, crosslinkers, their composition, and additives to be included in the matrix. This allows them to be engineered more precisely than other adsorbents to be most effective at adsorbing their intended pollutants. This flexibility, however, requires researchers to be more conscious regarding which chemicals and polymers are chosen to use in synthesis as many products can be cost prohibitive or environmentally taxing to produce. As previously discussed, polymers including lignin and corn zein are byproducts of existing industries and their application in bioremediation is an effective method of biomass valorization with little precursor treatments. In contrast, polymers like pectin and chitosan are also industrial byproducts but require some intermediate treatment steps before their applications in materials such as hydrogels. These polymers can be incorporated into hydrogels, but attention must be taken to make their application environmentally friendly.

Biomass application to environmental remediation is a large category of materials which are characterized by their chemical compositions, previously subjected treatments, and their origin materials. As presented here, sometimes these materials are pre-treated either physically or chemically to optimize adsorption.

Biochar can be synthesized from various biological materials but are often most environmentally friendly when synthesized from biomass. Biochar is unique when compared to hydrogels and raw biomass in bioremediation as it shares the benefits of valorizing biomass and is cheaper to produce than hydrogels. These benefits demonstrate why biochar has been much more extensively researched in bioremediation and especially in estrogen adsorption. Biochar research tended to date much further to the beginning of the millennium than biomass research when reviewing literature regarding estrogen adsorption. Thus, research is more plentiful regarding their adsorption capabilities and presents results much more promising than bioresidues or hydrogels. Drawbacks of biochar implementation in remediation however largely emanate from their synthesis and desorption procedures as these are often energy-intensive and time consuming. Maintaining temperatures at hundreds of degrees Celsius requires significant energy input which must be repeated to remove the pollutants from the biochar after use. This can be contrasted with hydrogels which are often desorbed using mild solvents or raw biomass where their replacement is not energy intensive. Thus, biochar is unique in its high adsorption efficiency due to its years of research and use of biomass input but requires large amounts of energy to synthesize and remove pollutants from it after adsorption.

Application of a given adsorbent for bioremediation will likely depend on the unique set of circumstances of each given application. While biochar is often effective in application, its energy-intensive synthesis can make it not very environmentally friendly. By contrast, the location of a given application may offer biomass that can be a very

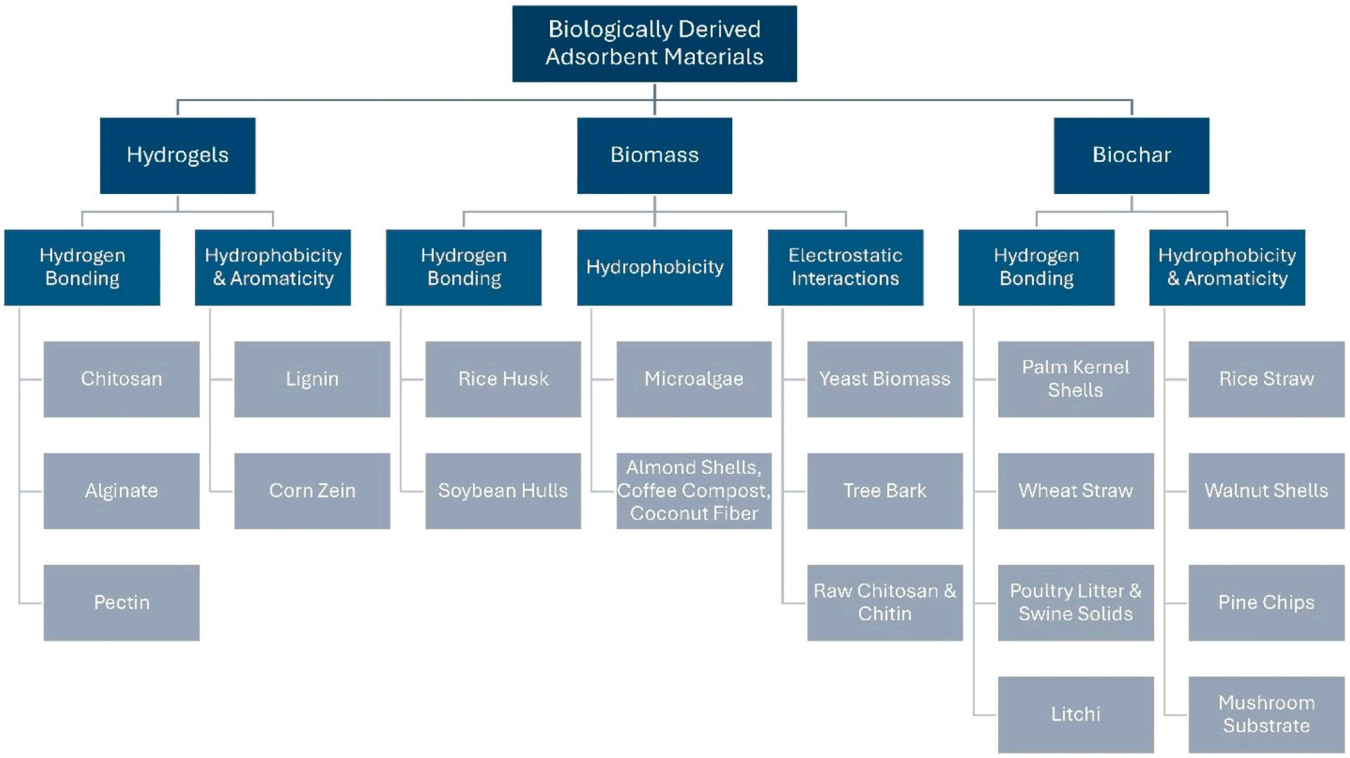


Fig. 2. Flowchart summarizing the currently reviewed adsorbent materials by type and adsorption mechanism.

Table 4
Summary of some common adsorption results.

Novel Results	Effect	Ref.
Chitosan nanoparticle interactions with EE2	High adsorption efficiency due to abundant amine groups available for hydrogen bonding with EE2	[25]
Introduction of corn zein into hydrogels	Improvement of adsorption of steroids due to the hydrophobicity and aromatic functional groups of zein protein	[20]
Introduction of lignin into hydrogels	Improvement of adsorption of PN through aromatic and carboxylic functional groups	[33]
Identification of lignin composition that improves steroid adsorption	Lignins more abundant in carboxylic and phenolic functional groups adsorb steroids more efficiently than lignins more abundant in hydrocarbon chains	[16]
Efficacy of naturally occurring fibrous internal structures	Steroids were effectively adsorbed onto unmodified tree bark particles due to abundant hydroxyl and aromatic functional groups presented from fibrous network	[6]
Competition between steroids for adsorption onto cellulosic materials	E1/E2/E3 do not compete when adsorbed onto materials with adsorption mechanisms consisting of cellulose, hemicellulose, and lignin	[32, 42]
Effects of pyrolysis temperatures on steroid adsorption	Higher pyrolysis temperatures increase steroid adsorption due to higher hydrophobicity and more aromatic functional groups	[55, 107]

effective adsorbent of a given pollutant which may make it highly favored. Finally, hydrogels demonstrate the most promising potential for remediation but require more research and development. If more time and attention can be invested in optimizing hydrogels to absorb estrogens, their benefits may outweigh the applications of biomass or biochar in the future. By focusing research on improving hydrogels economically, environmentally, and efficacy, they can present a strong path forward for remediating estrogen pollution in the environment.

6. Conclusion and future perspectives

The complexity in the development of hydrogels for bioremediation therefore necessitates more research and development than other adsorbents and this is exemplified in adsorption of estrogens as presented here. Few articles have been published exploring the adsorption of estrogen onto hydrogel matrices which makes their optimal efficiencies unknown given the lack of research. The required research and development also make hydrogels a more costly endeavor than more simple adsorbent materials and can limit their applications to situations where other adsorbents aren't suitable or until costs are reduced from research, and thus further research focusing on improving hydrogel adsorption efficiency of estrogens and reducing their costs of production are necessary to push their application forward.

Provided the life cycle analyses of each category of adsorbent material, their performances, and their unique benefits, it is likely that hydrogels and modified biomass will become the most sustainable and performan adsorbent materials of steroid pollution moving forward. While the use cases of various biomasses are less frequent, when a proper biomass is selected and implemented in a system that allows it to have a high adsorption efficiency, the drawbacks of development cannot outweigh the benefits of easy implementation and byproduct valorization. In other scenarios, it is likely that hydrogels designed in an environmentally friendly manner to efficiently adsorb pollutants will be the most favorable option in the future.

CRediT authorship contribution statement

Marie-Josée Dumont: Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Trevor Bell:** Writing – original draft, Conceptualization. **Jason Tavares:** Writing – review & editing, Supervision.

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.

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Data Availability

Data will be made available on request.

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