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Review

# Bisphenol A in Water Systems: Risks to Polycystic Ovary Syndrome and Biochar-Based Adsorption Remediation: A Review

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Access to clean and safe water sadly remains an issue in the 21<sup>st</sup> century. Water reservoirs, whether groundwater or surface water, are routinely contaminated by various harmful Emerging Contaminants (ECs). One of most prevalent pollutants among these pollutants is Bisphenol A, which is classified as an Endocrine Disrupting Compound (EDC). This substance adversely interferes with the endocrine system, primarily by mimicking estrogen, and has been considered a potential contributor to Polycystic Ovary Syndrome (PCOS) with 82.70% of 1,391 women studied showing a positive correlation between BPA exposure and PCOS. PCOS is currently the most prevalent endocrine disorder affecting women of reproductive age; however, its pathogenesis remains unclear, complicating diagnosis and subsequently patient care. In this review, these topics are thoroughly examined, with particular emphasis on biochar, a new promising method for large-scale water purification. Biochar, derived from various organic waste materials, has emerged as a cost-effective substance with remarkable adsorption properties achieving up to 88% efficiency over four cycles of reuse, similar to that of activated carbon. This review interrogates the suitability of biochar for counteracting the issue of EDC pollutants.

Keywords: Endocrine Disrupting Compounds • Bisphenol A • Polycystic Ovary Syndrome • Biochar • water pollution

# 1. Introduction

In recent years, the study of water pollution has become increasingly relevant as access to clean water is increasingly a cause for concern worldwide [1]. It is crucial to recognize that water is a dynamic system; therefore, pollutants are dispersed into all aspects of human life [2]. In this context, it is essential to draw attention to Endocrine Disrupting Compounds (EDCs). EDCs, despite having diverse chemical structures, share the common trait of interfering with normal endocrine function. These compounds are commonly found in a variety of products such as food sources, personal care products, pharmaceutical and hospital wastes, in addition to plastic materials and pesticides. Consequently, individuals can easily exposed to EDCs through air, soil, and water [3]. In the context of EDCs and their potential for harm, it is important to discuss Emerging Contaminants (ECs). ECs represent a diverse array chemical substances for which concerns have been raised only recently regarding their effect on human health and the environment [4]. Consequently, in the past these compounds were extensively employed in everyday manufacturing, and their presence in the environment was not adequately monitored or controlled by authorities. It is for this reason that one of the primary contributors to water pollution derives from conventional wastewater treatment plants (WWTPs) lacking specific technologies for identifying and degrading ECs [5].

Among ECs, one of the most well-known and prevalent of these contaminants is Bisphenol A (BPA). BPA is a plasticizer that has been used for decades as a monomer in polycarbonate plastic and epoxy resin. However, its toxic effects on human reproduction and its interference with the endocrine system have led to its classification as an EDC, and it was the subsequently banned by the European Food Safety Authority (EFSA), initially from plastic products for infants in 2011 and later from thermal paper in 2020 [6]. In the domain of EDCs, Polycystic Ovary Syndrome (PCOS) is one of the most studied and prevalent among endocrine-metabolic diseases among women of reproductive age [7,8]. PCOS is correlated with several health conditions such as stress, obesity, and diabetes, and can frequently lead to infertility and pregnancy complications [9]. Despite its prevalence, the exact causes of PCOS are not yet clearly understood. Of note, numerous studies have explored the correlation between the onset of PCOS and EDCs. These studies have shown that the level of Bisphenol A (BPA) in the serum of PCOS patients is higher than that observed in healthy women [10-12]. In 2024, Urbanetz et al. highlighted in their review the positive correlation between BPA exposure and the onset of PCOS. Their conclusion is supported by data

from 1,682 patients across more than 10 different countries [13]. Additionally, Hussain *et al.* [14] summarized outcomes defining the connection between PCOS and EDCs. With this in mind, research has concentrated on exploring new and effective approaches to address the shortcomings in wastewater treatment [15]. In the field of removing ECs and EDCs, chemical oxidation processes, electrochemical methods, microbial techniques, and in particular adsorbent materials, have been considered [16]. The special attention given to adsorbent materials is attributed to their low cost, efficiency, broad applicability, and ease of use. Among them, activated biochar is widely employed [15,17]. In detail, biochar represents a novel, environmentally friendly, and efficient medium for purifying water environments by absorbing ECs. Numerous emerging biomass-based biochars have been synthesized, derived from a variety of waste materials including banana peel, bamboo, spruce and corn straw [18– 20]. After the synthesis they are easily activated through additional chemical or physical treatments to enhance their performance [20,21]. These bio-based materials are very promising, yet still represent a challenging topic of study for researchers. They are not only efficient adsorbent materials but also hold promise in degradation processes [21]. They can adsorb multiple pollutants simultaneously, such as BPA and various metal cations, without a significant loss in adsorption efficiency [22].

This review explores how, despite the measures taken by safety authorities over the years, BPA remains a persistent danger to human health. Specifically, we examine the interaction of BPA with hormone regulation and its potential role in the onset of conditions like PCOS. Additionally, we highlight some promising eco-friendly carbon materials that show potential for removing BPA from the environment. The main topics already discussed in recent review are summarized in Table 1.

Table 1. Main subjects of recent reviews on PCOS and biochar as adsorbent material.

Review title	Review Topic	Key findings	Ref.
Bisphenol A and polycystic ovary syndrome in human: A systematic review	Demonstration of relationship between exposure to BPA and PCOS.	Positive relationship between exposure to BPA and PCOS was described in 19 studies (1391 [82.70%] of the PCOS patients)	[13]
Exploring the connection: endocrine disruptors and polycystic ovarian syndrome	The role of EDCs specially BPA in the pathogenesisis of PCOS	EDC exposure, especially BPA, may contribute towards PCOS by altering androgen synthesis, adipocyte stimulation and epigenetic modification.	[14]
Unlocking the potential of magnetic biochar in wastewater purification: a review on the removal of bisphenol A from aqueous solution	Highlight the efficiency of magnetic biochar for BPA removal from aqueous solution	Analysis of the use of plant-based magnetically induced biochar adsorbents for eliminating BPA from aqueous media. The most widely applied techniques for synthesizing magnetic biochar are thoroughly summarized	[21]

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Isabella Chiarotto graduated in Chemistry and Pharmaceutical Technology at Sapienza University of Rome. Researcher at the Chemistry Department of Sigma Tau Pharmaceutical Industry Spa-Pomezia (1989-91). In 1996 she attended research training at Ecole Normale Supérieure in Paris. She is currently associate professor of Chemistry for





Engineering at Sapienza University. Her research interests are mainly focussed on electrochemical studies and applications in organic syntheses.

# 2. An Overview of Bisphenol A

Bisphenol A, also known as 2,2-Bis(4-hydroxyphenyl)propane, is a biphenolic compound synthesized for the first time by the Russian chemist Aleksandr P. Dianin in 1891 by combining phenol with acetone under acidic conditions. Subsequently in the 1950s it was discovered that BPA reacts with carbonyl chloride to obtain a hard resin known as polycarbonate [23]. Moreover, BPA has been used for decades in the manufacturing of polycarbonate plastic and epoxy resin, consequently these polymeric materials are commonly used in the production of everyday reusable plastic items, including tableware and bottles. Furthermore, they are present in products intended for infants such as bottles and toys, in addition to disposable plastic items such as food film and packaging. BPA has applications in the production of thermal ink, paper, and textiles, making daily exposure practically inevitable [6]. (Figure 1)



Figure 1. Chemical structures of BPA, polycarbonate plastic and epoxy resin. Everyday essentials made from BPA plastic materials.

BPA has been designated by the European Chemicals Agency (ECHA) as a Substance of Very High Concern (SVCHC) due to its classification as an EDC, primarily due to its toxicity and adverse effects on human reproduction. Additionally, as of November 2023, BPA has been categorized as very toxic to aquatic life and very toxic to aquatic life

with long-lasting effects [24]. Nonetheless, BPA is not classified as a Persistent Organic Pollutant (POP) due to its volatility and its relatively short half-life in water and soil (approximately 4.5 days) [23]. Its presence in the air is primarily linked to its interactions with solid particulates in the atmosphere.

#### 2.1. BPA as water pollutant

As mentioned above, ECs are chemical compounds that lack, or have only recently obtained specific regulations, due to their impact on human health and the environment and were not been recognized as harmful [4,25]. This chemical class includes pharmaceuticals, pesticides, preservatives, and personal care products, that have detrimental effects on human health, ranging from promoting cancer development to causing issues with thyroid function and fertility [26,27]. BPA serves as a prime example of ECs due to effect on the endocrine system [28]. The EU has implemented restrictions, banning BPA from thermal paper and ink, in addition to baby bottles and toys intended for children under three years. Moreover, restrictions on BPA levels have extended to other plastic products, such as plastic food containers with a stringent limit of 0.05 mg/kg [24]. BPA ingestion frequently occurs due to its widespread presence in water reservoirs, with BPA being the most abundant EDC in groundwater and surface water [2].

As mentioned above, BPA is primarily used as an intermediate for synthesizing epoxy resin and polycarbonate plastics. Ideally, it should not be present in the environment as a free molecule. However, during industrial polymer production, a significant amount of BPA remains unreacted. These free molecules become trapped in the polymer lattice and can easily leach into the water when the plastic material is in prolonged contact with it [29]. Moreover, a study conducted in plastics industry areas in China demonstrated that there is a higher concentration of BPA in the water near production sites. This is due to the overproduction of BPA compared to its actual use in plastic manufacturing, leading to increased release of BPA into the environment as waste [30].

BPA enters in water cycle via different pathways including plastic manufacturing plants, fumes of waste incinerators, leachates from landfills and the effluents of conventional WWTPs [31]. Furthermore, BPA released into the atmosphere can precipitate into ground or surface water through rainfall [32]. Similarly, WWTPs lacking proper remediation systems for BPA can release it into groundwater [1,5,33]. Given the widespread contamination of water systems by BPA, humans are often exposed to high levels both through exposure to contaminated water, or through the diet by eating contaminated foods such as meat and fish (Figure 2) [34].

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Figure 2. The dispersion of BPA in the water cycle.

#### 3. PCOS outline

PCOS is a complex and heterogeneous endocrine disorder with an etiology that is not entirely understood [35]. Patients with PCOS exhibit a variety of symptoms, including polycystic ovarian morphology (PCOM), menstrual cycle disorders like oligo- or anovulation, and hyperandrogenism (HA) which is typically characterized clinically by the presence of acne, hirsutism, and alopecia [36]. Over the past 30 years the global prevalence of PCOS has increased and is particularly prevalent in high domestic income countries such as Italy, Japan, Australia, and New Zealand. The global prevalence of PCOS is discussed in further depth in an excellent review by Gao et al. [37]. Biochemical hyperandrogenism is characterized by elevated levels of testosterone and free testosterone, and is often associated with metabolic factors such as insulin resistance (IR), and compensatory hyperinsulinemia [2]. Consequently, individuals with PCOS have a higher risk of developing several comorbidities such as type-2 diabetes, obesity, and cardiovascular problems [7,12,38]. Diagnosis of PCOS is typically obtained by application of the Rotterdam criteria, initially described in 2003 at the Rotterdam conference between the European Society for Human Reproduction and Embryology and the American Society for Reproductive Medicine [39]. As per the Rotterdam criteria PCOS patients present at least two of biochemical and/or clinical hyperandrogenism, oligo or amenorrhea, and PCOM, the combination of these clinical features resulted in four phenotypes, termed A, B, C, and D [36,40]. Phenotypes A, B, and C exhibit hyperandrogenism and a tendency towards obesity, insulin resistance (IR), metabolic syndrome. In contrast, phenotype D patients are normoandrogenic and do not usually present with the abovedescribed metabolic conditions [41]. It is intriguing to note that IR is often viewed as not merely a symptom but as a causal factor that can contribute to the onset of PCOS [42]. IR is a condition characterized by cells exhibiting an inadequate response to insulin. This state of hyperinsulinemia can trigger heightened androgen production, elevated levels of free testosterone, and hindering follicular growth, consequently resulting in disturbances to ovarian function. The accumulation of insulin is also associated with an inhibition of lipolysis, leading to high obesity rates among insulin resistant patients with PCOS [43]. (Figure 3)

It is notably that no standardized protocol is applicable to all women diagnosed with PCOS. Consequently, the clinical approach must be tailored, focusing on addressing the unique combination of symptoms presented by the patient and prioritizing their immediate needs [36]. Adopting a healthy diet rich in fibers and low in saturated fats and carbohydrates, coupled with regular exercise, is the first recommended treatment for PCOS [44]. This is especially effective in hyperandrogenic patients due to the metabolic abnormalities seen in these patients. Insulin sensitizers such as inositol and metformin have shown demonstrable success in hyperandrogenic patients, causing a reduction in insulin and androgen levels leading to an improvement in ovarian function [45]. Pharmacological intervention with Oral

Contraceptive Pills (OCPs) are routinely used in PCOS, especially when patients are not seeking pregnancy, as these drugs help regulate menstrual cycles and androgen levels [46]. However, given the known metabolic risks associated with OCPs, some caution should be used when prescribing such medicines to PCOS patients, who are at a high risk of developing metabolic and cardiovascular complications [47].

Finally, Sadeghi *et al.* summarized three possible external factors that may play a role in the pathogenesis of PCOS: epigenetic mechanisms, inheritable alterations in genome and gene expression without changes in DNA sequences; environmental toxicants such as EDCs and advanced glycation end-products (AGEs); and physical and emotional stress related to mental health, in addition to dietary habits [35].

PCOS (Polycystic ovary syndrome)					
POSSIBLE EXTERNAL FACTORS	•EDCs (Endocrine disrupting compounds)				
	<ul> <li>AGEs (Advanced glycation end-products)</li> </ul>				
•Emotional stress					
	•Dietary habits				
SYMPTOMS:	•Genetic factors				
<ul> <li>Ovarian cysts</li> <li>Disruptions to the menstrual cycle (Infertility and challenges in sustain -Clinical hyperandrogenism (acne, hirsutism and alopecia)</li> <li>Biochemical hyperandrogenism (high levels of testosterone and free -Insulin resistance (obesity and cardiovascular problem)</li> </ul>	PHENOTYPES: Hyperandrogenic (A, B and C) Normoandrogenic (D)				
Th	ierapeutic options:				

Hyperandrogenic PCOS: lifestyle adjustment, insulin sensitizers, ovulating agents, combined oral contraceptives. Normoandrogenic PCOS: lifestyle adjustments, combined oral contraceptives, ovulating agents.

Figure 3. Overview of potential causes, common symptoms and managements of PCOS.

#### 3.1 BPA Mechanism of Action and Health Effects

BPA can reach the metabolism through different pathways: ingestion, skin contact and inhalation, with ingestion being the most common

route [34]. BPA is a lipophilic organic compound (log P 3.41), which is absorbed into the gastrointestinal tract upon ingestion [48]. When BPA is metabolized, it undergoes conjugation with UDP-glucuronic acid, forming BPA-glucuronide facilitated via uridine diphosphateglucuronosyltransferase, allowing for excretion via urine and feces. This metabolic process is considered a form of biological detoxification as BPA-glucuronide does not exhibit any disruptive activity [34]. However, toxicity can occur due to the  $\beta$ -glucuronidase enzyme, which can cleave the glucuronide group from the metabolite via hydrolysis, facilitating the release of the free active form of BPA into the bloodstream [38]. Research conducted by Pivonello et al. elucidated that BPA negatively affects the endocrine system, leading to adverse effects on reproductive health [38]. This is primarily facilitated by its ability to mimic estrogen, thereby stimulating estrogenic functions within the body. BPA possesses a conformational structure that allows it to bind to Estrogen Receptors (ER), thus activating them in a manner similar to estradiol. While it is true that BPA exhibits a lower affinity to ER compared with the natural hormone 17-beta estradiol, it is interesting to note that this affinity significantly increases when BPA is present at nanomolar concentrations [23]; therefore, this phenomenon may affect regular ovulation, in addition to endometrial growth and thickness [11].

BPA is also associated with an overproduction and secretion of androgens, in addition to an increase in free testosterone levels. This is attributed to its interference with testosterone 2a-hydroxylase and testosterone 6b-hydroxylase enzymes, in addition to BPA having a strong affinity for sex hormone-binding globulin (SHBG). BPA is further linked to insulin resistance (IR) due to its involvement in the release of interleukin-6 (IL-6) and tumor necrosis factor  $\alpha$  (TNF $\alpha$ ), while simultaneously inhibiting the release of adiponectin, a beneficial adipokine known to counteract insulin resistance (Figure 4a) [49]. In total, BPA is able to bind to several specific hormone receptors, in addition to recruiting key transcription factors involved in numerous processes from growth and differentiation to nutrient metabolism [23]. Consequently, BPA can play a role in numerous biological pathways including metabolic, cardiovascular, reproductive, in addition to cancer and immune system processes (Figure 4b).

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Figure 4. a) Health effects of BPA ingestion. b) Potential BPA molecular mechanisms in human as proposed by Cimmino *et al.* [23]. Reproduced with permission according to Creative Commons Attribution (CC BY) license.

#### 3.2 BPA Connection with PCOS

Having outlined the health complications of PCOS and briefly described the mechanism of action of BPA, it becomes evident that there may be a correlation between PCOS onset and prolonged exposure to BPA. In their review on the effects of BPA on women's health, Pivonello et al. presented a table summarizing the findings of several experimental studies examining the relationship between BPA exposure and the pathogenesis of PCOS [38]. These studies include an ex vivo investigation on human cells [50], in addition to two in vivo studies conducted on female rats [51,52]. In the first study conducted on human cells (Granulosa-lutein cells), it was established that cells exposed to increasing quantities of BPA led to an increase in matrix metalloproteinase (MMP)-9 output and activity, which in animal models could affect follicle growth, ovulation frequency, and oocyte guality [44]. Libertun et al. conducted a study on female rats that were exposed to various concentrations of BPA during neonatal development. They demonstrated that adult rats previously treated with BPA exhibited alterations in hormonal levels during adulthood, particularly an increase in testosterone and serum estradiol, along with a decrease in progesterone. Furthermore, they observed changes, including the appearance of PCOM, and disruptions in ovulation,

leading to infertility or subfertility, akin to what is typically observed in PCOS [51]. On this subject, Mukhopadhyay *et al.* have published an intriguing review exploring the correlation between alterations in the expression of 28 genes targeted by BPA and their association with PCOS dysregulation in both metabolic and endocrine pathways [53]. These results suggest that elevated levels of BPA in women diagnosed with PCOS contribute to hormonal dysfunction, as evidenced by clinical symptoms such as hyperandrogenism, decreased estrogen levels, ovulatory disorders, and follicle arrest, in addition to comorbidities like IR, compensatory hyperinsulinemia, and obesity. While it is beyond the scope of this review, BPA has been highlighted as a contributing factor to other health conditions such as depression, cancer, and immunosuppressive disorders, these are discussed in further detail in the recent review by Manzoor *et al.* [54].

# 4. BPA Removal from water

The widespread presence of BPA can be attributed primarily to the insufficient implementation of technologies in WWTPs, leading to contaminated water sources. Therefore, there is a need to discover not only to highly effective methods for detecting lower quantities of pollutants but also solutions capable of both detecting the contaminant and subsequently removing BPA [55]. In the field of

emerging contaminants, it is customary to employ adsorbent materials. Adsorption is a simple technique primarily based upon physical interactions [56], ensuring the removal of hazardous substances from aqueous environments without the formation of potentially toxic byproducts. The most used adsorbent for water pollutants is activated carbon, renowned for its high adsorption capacity attributed to its small particle sizes, large internal surface area, and active free valences [57,58]. Despite the various advantages of activated carbon, one notable drawback is its significant production costs. In recent years, numerous studies have focused on the development of biochar, an inexpensive material obtained from the thermal treatment of plant [59,60] or animal waste, with characteristics and performance comparable to activated carbon [15].

#### 4.1 Biochar synthesis and modification

Pyrolysis is the most common thermal treatment for biochar synthesis, which involves heating biomass, such as agrifood waste, at moderate temperatures (400-700 °C) in the absence of oxygen [61,62]. The conditions of pyrolysis, including temperature, pressure, heating rate, and residence time, significantly influence both the yield and properties of biochar [61]. For example, higher temperatures lead to an increase in the char surface area but a decrease in yield. Similarly, an increase in the heating rate results in higher porosity but a decrease in yield. The optimal method for obtaining high-quality biochar is known as "slow pyrolysis" [61,62]. The char isn't the sole product obtained from biomass pyrolysis; in addition to char, there are also liquid (bio-oil) and gaseous components. The proportional fraction of these products is determined by the conditions of pyrolysis. Slow pyrolysis yields a higher quantity of solid output (approximately 35%) compared to liquid and gaseous products. It involves low temperatures (550-950 °C), low rate of heating and a high residence time (5-30 minutes) [62].

In this context, Spagnuolo *et al.* in their paper focused on the synthesis of biochar from *Sargassum muticum*, extensively discussed how increasing temperature (180°C, 240°C, and 300°C) and residence time (60-300 min) influenced the physicochemical properties of the biochar [63]. A summary of their results is reported in Figure 5.

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👚 Temperature 1 Residence Time Decreasing of intensity band from 3000 cm<sup>-1</sup> and FTIR (Fourier 3700 cm-Increasing bands 2925 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> **Fransform** Infrared Decreasing of diffraction peak 15 20 Stronger peak at the 25.79 20 angle XRD (X-Ray Diffraction) SEM 1 Formation (Scanning Electron secondary hydrochar with polyaromatic structure Microscopy) Increasing amount of carbon along with a decreasing in oxygen XPS (X-ray toelect auantity Spectroscopy

Figure 5. Biochar's physicochemical properties depend on the temperature and residence time during its synthesis [63].

Feedstock for biochar production can consist of a wide range of organic solid waste, including agricultural and forestry residue, food waste, and sewage sludge. Moreover, this kind of production process is advantageous as it reduces waste, thereby contributing to environmental sustainability, thereby promoting more eco-friendly practices. The physicochemical properties of biochar, such as specific surface area, functional groups, and pore dimensions, are also influenced by the characteristics of the starting material. These characteristics can be further enhanced to be more absorbent through various techniques. The appropriate modifications are closely related to the chemical structure and properties of the pollutant that needs to be adsorbed. In fact, the aromaticity of the biochar can be increased to enhance  $\pi$ - $\pi$  interactions with aromatic ring contaminants, and this procedure also increases hydrophobic interactions with hydrophobic compounds. The surface polarity can be also increased to facilitate hydrogen bonding formation with pollutant molecules. Furthermore, alkaline or acid treatments of the biochar can enhance pore formation, allowing for better trapping of contaminants with larger chemical structures [64].

Cheng *et al.*, reported methods used to modify particle surfaces, including the use of metal oxides or salt, acid-base modifications, incorporation of clay into the biochar structure, and ball milling [17]. The use of metal oxides and salts enhances the electrostatic attraction and anion exchange capacity, facilitating the formation of various chemical bonds through the introduction of new functional groups. Surface modification with acids or bases is one of the most commonly used methods to enhance surface area and pore dimensions [65]. The introduction of hydroxy and carboxy groups on the surface is crucial for aiding the absorption process [66]. After clay modification, the biochar exhibits an increased porosity and enhanced compatibility

with the contaminant. Additionally, ball milling treatment allows for an increased physical adsorption capacity [67]. It has been observed that certain modified biochar variants can achieve a comparable absorption capacity to commercial activated carbon, while reducing production costs by half. Specifically for BPA removal, adsorption on biochar has proven to be highly efficient, especially when the surface is properly activated. This activation increases the possibility of forming  $\pi$ - $\pi$  interactions with the aromatic rings of the BPA and facilitates the establishment of electrostatic interactions or hydrogen bonds with hydroxyl groups [68]. (Figure 6)

Numerous studies investigating this topic.



Figure 6. Possible surface modifications to enhance pollutant adsorption.

Supong *et al.* synthetized activated carbon starting from Tithonia diversifolia (Tree marigold) with a maximum adsorption capacity of 15.69 mg g<sup>-1</sup> calculated with Langmuir isotherm model [69]. Biochar modified with Fe has been particularly effective. In detail, Xu and colleagues obtained biomass activated carbon (BAC) from cherry

Table 2. Biochar for Efficient BPA Removal.

stones, which was modified with FeCl<sub>3</sub> to create a composite BAC/FeOx capable of degrading 20 mg/L of BPA in only 5 minutes. The superior results obtained with Fe modification are associated with a higher surface area [70]. Furthermore, they demonstrated that the presence of Fe<sup>0</sup> and Fe<sub>3</sub>O<sub>4</sub> on the char surface can activate peroxydisulfate, which participates in the degradation mechanism of BPA as a free radical (SO4<sup>--</sup>) alongside OH<sup>--</sup> radicals from water [70]. Similarly, S. Tuomikoski's group produced a composite (Fe-CR) from carbonized wood (CR) chips (pine and spruce), demonstrating an experimental maximum adsorption capacity of 41.52 mg g<sup>-1</sup>. In addition, they also tested biochar treated with CaCl<sub>2</sub> (Ca-CR) and HCl (H-CR) [71]. Furthermore, Egbedina et al. synthetized a magnetic carbon material (Fe-EG) from carbonized eggshell by adding FeCl<sub>3</sub>, FeSO<sub>4</sub> to an alkaline aqueous solution of the carbonized eggshell, resulting in a maximum adsorption capacity of 35 mg g-1 [72]. Additionally, a reusable magnetic activated carbon with a maximum adsorption capacity of 207.77 mg g<sup>-1</sup> was obtained from carbonization of a mixture of shrimp shell with cellulose. In this instance, the biochar was activated with NaHCO<sub>3</sub> and treated with FeCl<sub>3</sub> and FeSO<sub>4</sub> to obtained the modified carbon material as a precipitate [73]. Zhang et al. acquired biochar through an alternative means by using pyrolyzed grapefruit peel, both modified and unmodified with FeCl3 and FeSO4, demonstrating excellent results in terms of BPA removal [74]. Moreover, very interesting results have been observed with sulfonated sawdust biochar, which demonstrated an excellent adsorption capacity of 263.75 mg g<sup>-1</sup>. This is particularly exciting because sawdust is a ubiquitous material, and after a simple thermal treatment with sulfuric acid, it can be transformed into a high-performance adsorbent for BPA comparable to commercial absorbents (Table 2) [75].

Biomass	Modifier	Adsorption capacity	Adsorbent dose	Contact time	Reusability	Ref.
Tithonia diversifolia	/	15.69 mg g <sup>-1</sup>	0.2 g	80 min	/	[69]
Cherry stone powder	$\operatorname{FeCl}_3$	20 mg/L	0.2 g/L	5 min	4 cycles	[70]
Wood chips (pine and spruce)	$FeCl_3$	41.52 mg g <sup>-1</sup>	5 g/mL	24 h	3 cycles	[71]
	CaCl <sub>2</sub>	16.84 mg g <sup>-1</sup>			/	[]
	HCI	23.84 mg g <sup>-1</sup>			/	
Eggshell	FeCl <sub>3</sub> , FeSO <sub>4</sub>	35 mg g <sup>-1</sup>	0.1 g	100 min	/	[72]
Shrimp shell	FeCl <sub>3</sub> , FeSO <sub>4</sub>	207.77 mg g <sup>-1</sup>	1 g/L	1 min	5 cycles	[73]

Grapefruit peel	/	88.01%	0.4 g/L	150 min	4 cycles	[74]
	FeCl <sub>3</sub> , FeSO <sub>4</sub>	94.74%			/	
Saw dust	H <sub>2</sub> SO <sub>4</sub>	263.75 mg g <sup>-1</sup>	10 mg / 20 mL	/	/	[75]

#### 4.1 Studies of BPA removal

When considering the adsorption mechanism of BPA on biochar, three types of interactions related to their chemical structures should be considered. The predominant intermolecular force is characterized by  $\pi$ - $\pi$  stacking interactions [74], which occur between the benzene rings of both the adsorbent and the adsorbate, facilitating strong molecular associations. During the activation process, carboxylic or carbonylic groups are formed on the biochar surface presenting sites capable of establishing hydrogen bonds with the hydroxylic groups of BPA, thereby facilitating further interactions and enhancing the adsorption process. This interaction was confirmed using Density Functional Theory (DFT) calculations in Tithonia diversifolia biochar. It was found that the strongest hydrogen bonding occurs between the oxygen of the BPA molecule and the hydrogen of the carboxylic group on the biochar [69]. An analogous mechanism has been proposed for sulfonated biochar, wherein -SO<sub>3</sub>H groups may form similar hydrogen bonding interactions [75]. An essential consideration for BPA absorption in biochar is pH, which can significantly influence the behavior of BPA. In acidic conditions, BPA hydroxylic groups become protonated, while in basic environments BPA exists as an anion; hence, the formation of charged species can facilitate electrostatic interactions with the biochar surface [71,75]. This phenomenon notably increases the adsorption capacity of biochar for BPA molecules. It is imperative to recognize that biochar is a porous material, capable of adsorbing pollutant molecules by the filling of pores [73]. This characteristic should not be overlooked, as it significantly contributes to the overall adsorption capacity of biochar for pollutants like BPA (Figure 7).



Figure 7. Mechanisms involved in BPA adsorption on biochar surface.

Recently, nanocomposite derived from tannery sludge and zinc oxide (ZnO) nanoparticles demonstrated high efficiency in reducing the concentration of BPA in aqueous solutions under visible light irradiation through a combination of adsorption and photocatalytic degradation mechanisms [76]. Beside this, the reaction mechanism of BPA degradation by NCM-0.6/PMS system is reported by H. Chen *et al.* where the synergistic effect of adsorption and oxidation is the key to the rapid removal of BPA [77].

In total, these recent studies highlight the global concern of endocrine-disrupting chemicals like bisphenol A (BPA) in aquatic environments and the growing interest in biochar as an eco-friendly, cost-effective adsorbent for wastewater treatment.

#### 4.2 Reusability and regeneration of biochar

In the age of green chemistry, the reusability of materials is often a high priority, as is the case for biochar. When biochar is used as an adsorbent, it is appropriate to discuss the regeneration of the material. Regeneration involves desorbing the adsorbate from the adsorbent, which can be accomplished through various methods. This can be achieved through thermal means [61], or alternatively, the char can be washed with organic solvents such as methanol or ethanol [70,75]. It has been demonstrated that the adsorption capacity doesn't significantly decrease over multiple uses, allowing biochar to be efficiently utilized for 4-5 cycles [73]. Similarly, when magnetic biochar is used as a catalyst, it can be reused with satisfactory results for up to four cycles after applying an external magnetic field and washing it with water [71]. In this context, it is necessary to consider the cost of regenerating biochar compared to its production costs [61]. It's worth

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noting that biochar is commonly derived from various sources including agricultural, food, forestry wastes, and municipal sludge. Importantly, the production cost is approximately half that of commercial activated carbon while delivering comparable performances [15]. Furthermore, as mentioned earlier, the pyrolysis process also yields bio-oil and biogas, which contribute to the energy recovery process, and can be utilized for other beneficial purposes [78–81].

Furthermore, the generation of secondary waste can be considered a problem, but spent adsorbents could be successfully employed as fertilizers instead of synthetic ones. Additionally, biochar incineration can be useful for the production of thermal energy, replacing coal and limiting the formation of toxic gas emissions [82]. These additional uses for spent adsorbents further enhance the appeal of waste-derived biochar.

# 5. Conclusion

In conclusion, this review underscores the water pollution stemming from the inadequate WWTPs. BPA in particular has been highlighted as a course for its concern due to its link to PCOS and other endocrine disorders. While further studies are required to establish the link between BPA and PCOS, the various removal methods presented herein offer hope at reducing systemic exposure to these pollutants. Biochar offers an economical alternative to activated carbon, with potential to serve as valuable resource for water purification efforts and address waste disposal challenges.

#### 6. Future perspective

In the field of contaminant adsorption, many promising results have been achieved, but much work remains to be done. It is particularly important to continue investigations to improve synthesis methodologies, with the aim of minimizing the need for postsynthesis functionalization. Additionally, a key aspect that needs improvement is conducting experiments on a large scale to test the scalability of biochar and move biochar beyond laboratory settings and into industrial applications. Moreover, for these adsorbents to be used on an industrial scale, it is crucial to perform selectivity analyses for specific pollutants in complex water samples that closely resemble real-world conditions. Regarding the effect of contaminants such as BPA on human health, further work is required to understand the complex biological mechanisms that underpin affected conditions. In the case of PCOS, this is complicated by the multifactorial nature of the syndrome; however, the identification of possible environmental risk factors represents a unique research space that will benefit prevention methods in years to come.

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# **Author Contribution Statement**

Conceptualization, C.M. and S.H.M., methodology, S.H.M., writing– original draft preparation C.M., writing–review and editing, C.M. and S.H.M., supervision I.C. All authors have read and agreed to the published version of the manuscript.

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#### **Entry for the Graphical Illustration**



# **Twitter Text**

Access to clean water is challenging. Bisphenol A (BPA), an Endocrine Disrupting Compound, mimics estrogen and is linked to Polycystic Ovary Syndrome (PCOS). This review explores BPA's role in PCOS and suggests biochar for water purification.