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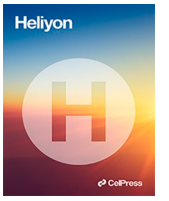

Review article

The use of agro-waste-based adsorbents as sustainable, renewable, and low-cost alternatives for the removal of ibuprofen and carbamazepine from water

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A B S T R A C T

The occurrence of residual pharmaceuticals in the aquatic environment poses major toxicological impacts and adds to the increasing pressure on water resources. Many countries are already suffering from water scarcity, and with the burdening costs of water and wastewater treatment, the race towards innovative sustainable strategies for pharmaceutical remediation is ongoing. Out of the available treatment methods, adsorption proved to be a promising, environmentally friendly technique, particularly when efficient waste-based adsorbents are produced from agricultural residues, thus maximizing the value of wastes, minimizing production costs, and saving natural resources from depletion. Among the residual pharmaceuticals, ibuprofen and carbamazepine are heavily consumed and highly occurring in the environment. This paper aims to review the most recent literature on the application of agro-waste-based adsorbents as sustainable alternatives for the removal of ibuprofen and carbamazepine from contaminated waters. Highlights on the major mechanisms implicated in the adsorption of ibuprofen and carbamazepine are presented, and light is shed on multiple operational parameters that hold a key role in the adsorption process. This review also highlights the effects of different production parameters on adsorption efficiency and discusses many limitations currently encountered. Finally, an analysis is included to compare the efficiency of agro-waste-based adsorbents relative to other green and synthetic adsorbents.

1. Introduction

Stress on the world's water supply is alarmingly escalating with population growth, industrialization, urban expansion, and over-exploitation of water resources [1,2,3,4,5]. Half a billion people in the world are already facing severe water scarcity all year round, and numbers are expected to extend to 2.8 billion people in 48 countries by 2025 [4].

Beyond the physical aspect of water scarcity, the quality of the available water is degrading due to the numerous anthropogenic practices [3], generating and discharging a myriad of organic and inorganic pollutants. Pharmaceuticals are among the organic

Abbreviations: WHO, World Health Organization; NSAID, Non Steroidal Anti-Inflammatory Drug; AOP, Advanced Oxidation Process; COF, Covalent Organic Framework; MOF, Metal Organic Framework; GONP, Graphene Oxide Nanoplatelet; CMNT, Carbon-dot and Magnetite-modified carbon Nanotube; AC, Activated Carbon; SBG, Spent Brewery Grain; WAB, Wood Apple Biochar; WASAB, Steam Activated Wood Apple Biochar; SCW, Spent Coffee Waste; P-BC, Plane tree leaf- Derived Biochar; PS, Pepper Stem; PFO, Pseudo-First Order; PSO, Pseudo-Second Oder.

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pollutants that find their way to the environment mainly through sewage effluents, pharmaceutical industry discharges, illicit dumping, and excessive use of veterinary drugs in the agricultural industry [6,7,8].

Almost half of the pharmaceutical wastewater produced globally is discharged without specific treatment [6]. Multiple factors combine to sustain a continuous input of pharmaceuticals into environmental waters, namely the lack of safe disposal methods, routine monitoring, and management regulations, along with the inefficiency of conventional wastewater treatment methods to remove pharmaceutical residues [8]. This has led to the occurrence of more than 600 active pharmaceutical ingredients (APIs) and their metabolites in the environment of 71 countries worldwide [9].

Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID) with analgesic and antipyretic effects and is listed among the essential medicines by the World Health Organization (WHO) [10,11,12]. Globally, it is the third most consumed drug [13], and the second most manufactured with a production rate of 15,000 tons/year. Ibuprofen recorded the highest concentrations in wastewater treatment plant effluents [14] reaching up to 25 $mg.L^{-1}$ [15]. The drug displayed inhibitory effects on the microbiota of activated sludge through the decrease of bound extracellular polymeric substances and the reduction of the microbial oxygen uptake [16,15]. Moreover, ibuprofen is presumed to be an endocrine disruptor in human and wildlife [17,18]. It is implicated in decreased testosterone secretion [19] and elevated estradiol levels in the plasma of exposed male fish [20]. Due to its lipophilicity, it is capable of bioaccumulating in the fatty tissues of living organisms [21]. Carbamazepine, equally listed as an essential medicine by the WHO [12], is an anti-epileptic and anticonvulsant drug used to prevent seizures [22]. It is also a psychotropic agent for the treatment of schizophrenia, depression, and certain pain syndromes [23]. More than 1000 tons of annual carbamazepine consumption has been reported globally, and it is estimated that around 30 tons of carbamazepine are discharged into water bodies per year [24,25], making it the most frequently detected pharmaceutical along with diclofenac [26]. Clara and co-authors qualified carbamazepine as a suitable wastewater marker for anthropogenic influences in aquatic environments due to its persistence [27]. It has been used as a tracer to calculate the elimination rate of other pharmaceuticals in rivers [28]. Carbamazepine was detected in surface waters at 1.075 $\mu g.L^{-1}$ in Berlin, at levels up to 1.1 $\mu g.L^{-1}$ in groundwater samples [29], and at alarming concentrations ranging from 10 to 443 $mg.L^{-1}$ in pharmaceutical industry effluents. Carbamazepine showed toxicity to aquatic invertebrates, bacteria, fish, and algae, and may be responsible for severe side effects in humans. Acute and chronic toxicity effects of carbamazepine on aquatic organisms were reported at concentrations higher than 25 $\mu g.L^{-1}$ [23].

The potential toxicity and the scarce water resources underscore the need to develop special methodologies and treatment processes for the removal of pharmaceuticals from wastewater [6,8]. The average removal efficiency of carbamazepine using conventional wastewater treatment was reported to be lower than 10% [30,25]. A mere 7% removal was reported by Ternes and coworkers [31]. Advanced Oxidation Processes (AOPs) based on different classes of oxidizing agents are among the treatment techniques. Ozone, peroxide, Fenton's reagent, and titanium dioxide are examples of highly reactive hydroxyl radicals involved in AOPs and are capable of degrading pharmaceuticals in a rapid and non-selective manner. Studies had reported a 12% removal of ibuprofen using ozonation and AOPs by O_3/H_2O_2 [32], and 70% using chlorine dioxide oxidation [33]. For carbamazepine, chemical oxidation proved to hold the highest removal efficiency. Hua *et al.* reported up to 99% depletion of carbamazepine after ozonation treatment [34]. Fenton's oxidation of wastewater, implicating ferrous and/or ferric cations to generate powerful oxidizing agents [35], achieved carbamazepine removal between 84 and 100% [36]. Shu *et al.* measured up to 90% removal of the pharmaceutical by UV/H_2O_2 oxidation [37]. However, by-products requiring further treatment are a major drawback that is encountered following AOPs, and oxidation processes are known to impose cost restrictions in full-scale wastewater treatment plants [38,39]. Membrane filtration technologies are also applied in the remediation of emerging organic contaminants. However, these are often restricted due to membrane fouling caused by the presence of other organic matter in the water being treated [40]. Other processes include biological degradation and phytoremediation, involving microbial digestion and plant extraction of the contaminants, respectively [41]. For instance, a 60% removal efficiency was achieved for carbamazepine following a 48 hour enzymatic treatment with fungal laccase, an enzyme from Trametes versicolor [23].

Given the limited efficiency of conventional activated sludge methods, and the major drawbacks of AOPs, removal of pharmaceuticals from contaminated wastewaters by physical techniques such as adsorption stands out as a promising option [42,43]. Characterized by high efficiency, ease of operation, and practically no release of any pharmaceutical derivatives [38,23], adsorption is a lower-cost alternative that can be used to limit the spread and bio-availability of pharmaceuticals in contaminated water. Further advantages of adsorption are achieved when utilizing agricultural waste as a primary source for adsorbent production. Agro-wastes are globally accessible [44], largely produced and discarded in all geographic areas. The productive conversion of these wastes into potential adsorbents valorizes them and precludes the need for planning their disposal strategies.

The focus of this review is on the adsorbents originating from agricultural waste and applied for the removal of two heavily consumed pharmaceuticals, i.e., ibuprofen and carbamazepine, from water. The discussion will tackle the production processes of the adsorbents, the operational parameters applied during the adsorption experiments, and how these affect the uptake capacity of the adsorbent. In addition, the properties of the pharmaceuticals and their potential mechanisms of interaction with the adsorbents are highlighted. Finally, the post-treatment and the recovery of spent adsorbents are considered in the context of "green" and "sustainable" chemistry.

2. Properties of ibuprofen and carbamazepine

The adsorption mechanism relies not only on the characteristics of the adsorbents, but also significantly on the properties of the adsorbate molecules [45]. The molecular size dictates the adsorbate's ability to access the porous structure of the adsorbent, the solubility and the octanol-water partition coefficient (Log Kow) are responsible for the hydrophobic interactions, and the dissociation

constant (pKa) controls the ionization state of the compound [46]. Indeed, the carboxyl group makes ibuprofen ionizable and available in its anionic form when the pH is greater than its pKa, and in its neutral form at pH levels below its pKa [47,48,49]. Moreover, the pH alters the surface charge of the adsorbent depending on its point of zero charge (pH_{pzc}). Thus, the electrostatic interaction between ibuprofen and the adsorbent is pH-dependent. Hydrogen bonding is known to substantially affect non-electrostatic interactions [50], and the carboxyl group in ibuprofen acts as both a hydrogen bond donor and a hydrogen bond acceptor [51]. On the other end, the phenyl ring in the structure of ibuprofen is responsible for attractive pi-stacking interaction with aromatic rings, if any are available on the surface of the adsorbent.

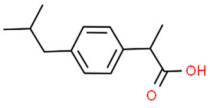
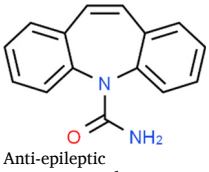
Carbamazepine is a basic, non-ionizable drug with a pKa value of 13.9. It is neutrally charged over the whole pH range [52,22,23], and is relatively lipophilic [53]. Carbamazepine is a persistent compound in sewage-water treatment plants [42,54]. Due to its high pKa value, the adsorption behavior of carbamazepine is not much dependent on the pH as much as on the surface chemistry of the adsorbent. Therefore, electrostatic interactions do not intervene in the adsorption process. However, the pH slightly affects the hydrogen bonding between carbamazepine and the adsorbent through the concentration of H^+ ions available in the solution. A low pH value leads to a more facile interaction between functional groups on the adsorbent and carbamazepine with H^+ due to the abundance of H^+ in the solution. This decreases hydrogen bonding between the adsorbent and carbamazepine and lowers the adsorption efficiency. Conversely, when the concentration of H^+ is reduced at a higher pH, the amide functional group (-NH2-C═O) of carbamazepine can more readily interact through hydrogen bonding with oxygen-containing functional groups of the adsorbent, leading to enhanced adsorption efficiency. Carbamazepine also carries aromatic rings in its structure favoring π-π interactions with the adsorbents also possesing aromatic rings in their composition. Therefore, the main identified mechanisms that contribute to carbamazepine adsorption are non-electrostatic interactions via hydrogen bonding and π-π interactions [24]. These structural considerations must be exploited when designing ibuprofen and carbamazepine-targeted adsorbents [49,50]. Table 1 shows the physicochemical characteristics of ibuprofen and carbamazepine [55,56,57,58].

3. Agro-waste based adsorbents for the removal of ibuprofen and carbamazepine

Numerous studies have shed light on the importance of adsorption in the treatment of wastewater containing pharmaceuticals using conventional synthetic adsorbents, and many novel adsorbents were synthesized for the removal of ibuprofen, carbamazepine, and other pharmaceuticals from water. Indeed, Covalent Organic Frameworks (COFs) [59], Metal-Organic Frameworks (MOFs) [60], graphene oxide nanoplatelets (GONPs) [61], hematite nanoparticles [23], carbon-dot and magnetite-modified carbon nanotubes (CMNTs) [22], composite iron nano adsorbents [62], functionalized magnetic multiwall carbon nanotubes [63], and magnetic nanoparticle coated zeolites [64] are among the synthetic adsorbents explored for this purpose. Porous carbon derived from MOF through pyrolysis at 1000 °C (PCDM-1000) showed exceptional efficacy in removing ibuprofen [60]. The maximum reported adsorption capacity was 320 $mg.g^{-1}$ which is the highest among the explored adsorbents.

Despite some of their excellent adsorptive properties, conventional adsorbents are not a viable option for pharmaceutical removal due to their high production costs. In line with the sustainable development of water purification techniques, green adsorbents emerged as competitive alternatives for conventional synthetic adsorbents for being widely available, inexpensive, and eco-friendly. Green adsorbents are recycled material obtained as by-products of, or residues from, biological, agricultural, and industrial sources as well as from forest industries. The essential properties defining a sustainable green adsorbent are mainly efficiency, production costs, and regeneration capacity. These become of utmost importance when scaling up the use of adsorbents from laboratories to water and wastewater treatment plants. Ideally, an efficient adsorbent must possess fast kinetics, as well as high surface area, porous features, adsorption capacity, and regeneration potential. Agricultural waste offers an accessible and renewable source of adsorbent precursors, and answers to the increasing need of sustainability in managing water and wastewater treatment strategies [65]. Agricultural wastes are the unwanted solid residues derived from agricultural activities, namely crops and livestock production. Lignocellulosic materials are a major component of agricultural wastes, consisting mainly of cellulose, hemicellulose, pectin, and lignin, in addition to proteins, lipids, starch, and simple sugars. The complex structure of lignocellulosic materials renders them poorly degradable [66,67]. However, they have demonstrated the capacity to adsorb both organic and inorganic contaminants due to their porosity and the abundance of

Table 1
Physico-chemical properties of ibuprofen and carbamazepine.

Pharmaceutical	Ibuprofen	Carbamazepine
Chemical formula	$C_{13}H_{18}O_2$	$C_{15}H_{12}N_2O$
Structure		
Therapeutic class	Nonsteroidal Anti-inflammatory Drug	Anti-epileptic
Molecular weight	206.28 $g.mol^{-1}$	236.27 $g.mol^{-1}$
Water solubility	21 $mg.L^{-1}$	18 $mg.L^{-1}$
pKa	4.91	13.9
Log Kow	3.97	2.45

functional groups on their surface [68]. For instance, lignin integrates aliphatic and phenolic hydroxyl groups, methoxyl groups, and carbonyl groups that may enhance its adsorptive performance [69].

The reviewed studies utilizing agro-wastes to produce adsorbents report their application either as the raw biomass, or as its chemically and/or physically modified form. Most commonly, the biomass is converted to activated carbon (AC) [70], which seems to be the most widely used [21,14], and the most promising in eliminating pharmaceutical residues from water [71]. ACs are characterized by a large surface area and high uptake capacity, as well as high porosity due to the evaporation of volatile compounds following pyrolysis [72].

3.1. Raw agro-waste biomass

Few studies reported the application of agricultural wastes in their raw untreated forms. Crushed knotweed leaves [73], cocoa-shells [74], waste rice straw [75], were used for ibuprofen and carbamazepine adsorption from water. Activation of the raw biomass is assumed to introduce functional groups onto the surface of the adsorbent as a means of enhancing the binding of target contaminants. For instance, Jean-Rameaux and coworkers compared the performance of the non-treated cocoa-shells to that of glycine grafted, plasma activated cocoa-shell fibers. Indeed, plasma activation introduced carboxyl, carbonyl and hydroxyl groups to serve as grafting sites for glycine on the cocoa-shell fibers. Notably, an increase in the maximum adsorption capacity from 24 to 39.15 $mg.g^{-1}$ was recorded [74]. The general preparation steps of the raw biomass that precede the adsorption experiments are detailed in Fig. 1.

3.2. Activated carbon

The use of activated carbon (AC) as an adsorbent dates back to the 18th century when charcoal was first employed to adsorb gases in 1773. Later in 1785, charcoal was applied in a liquid phase for the first time, and intended to remove dyes and decolorize various aqueous solutions [76].

Typically, ACs are produced from coal, peat, or petroleum coke [77], however, the high cost of commercially available ACs is a limiting factor [78,79,80,71,81], thus explaining the need to find sustainable alternatives from renewable sources such as agro-wastes. Using agricultural by-products for AC production is beneficial in the upcycling of waste, and can be tailored based on the available biomass in a given geographical area [72]. Fig. 2 illustrates the general steps involved in the production of AC from agricultural raw materials.

The process involves two consecutive phases starting with carbonization to rid the material of volatile and non-carbon compounds [82], followed by activation [83]. It is during the carbonization phase that the microcrystalline structure of the ACs starts to develop. ACs are non-graphitic carbons [84], they exhibit a well-developed porous structure, in contrast to the relatively less-developed porosity observed in graphitic carbons [76,85]. Some non-graphitic carbons may evolve to an ordered structure of crystalline graphite, where the graphene layers are oriented parallel to one another, upon heat treatments between 1700 and 3000 °C. These are known as graphitizing carbons. Conversely, non-graphitizing carbons cannot develop a graphitic structure, even at high-temperature heat treatment for up to 3000 °C [86]. The activation of the carbonized product involves either chemical processes requiring the use of chemical agents, i.e., KOH, H_3PO_4, and $ZnCl_2$, or physical/thermal activation implemented at high temperatures (800–1000 °C) using hot gases such as carbon dioxide or water vapor steams, or a mixture of both [87,82,83]. Physical activation combines lower costs and lower environmental impacts; however, the chemical process is preferred as it combines the carbonization and the activation phases in a single step, runs at lower temperatures (< 800 °C), and results in porosity improvement of the final material [88,76,82]. The activation step modifies the surface of the adsorbent through introducing new functional groups on its surface, which could be basic or oxygenated acid groups like carboxyl, lactone, phenol, and carbonyl [89]. Furthermore, the activation conditions, such as the degree of carbonization or the impregnation ratio of the activating agent to the adsorbent, are assumed to define the porous structure and the surface properties of the produced AC [90,91].

Functionalized bean husks, usually discarded as agricultural waste, were converted to AC and employed for the removal of

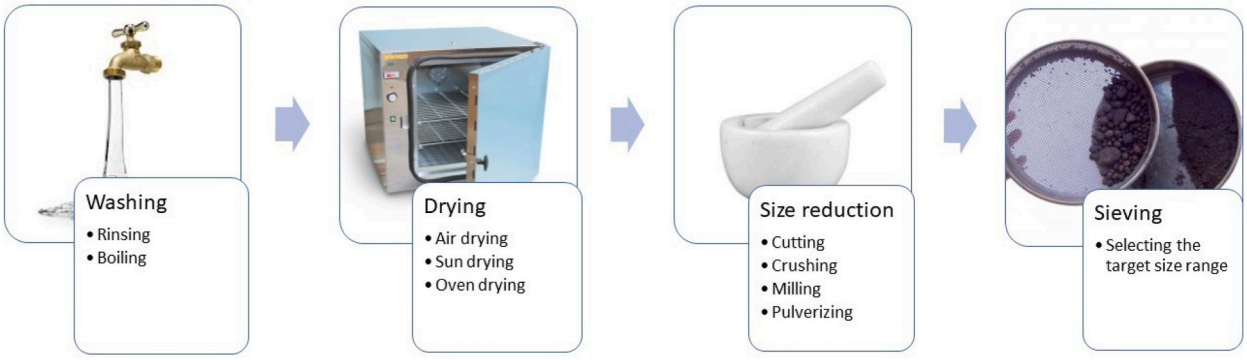


Fig. 1. Schematic diagram for the preparation of agricultural waste for adsorption experiments.

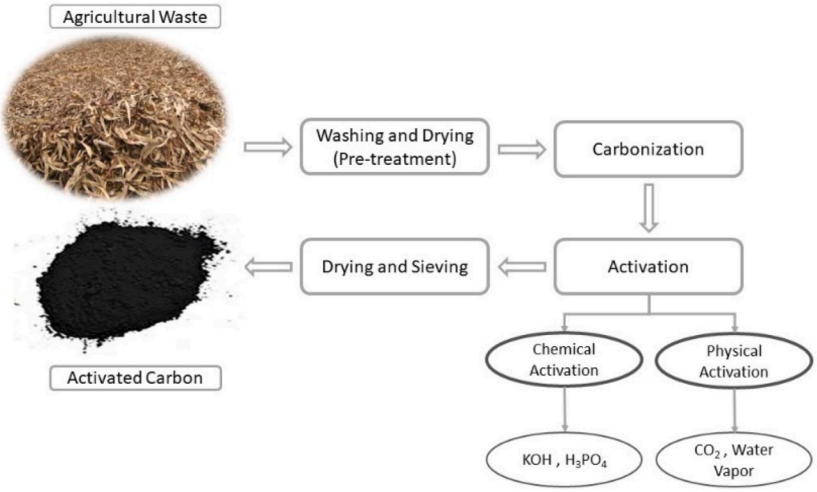


Fig. 2. Schematic diagram for the production of activated carbon from agricultural waste.

ibuprofen [92]. Converting bean husks to AC follows closely the steps presented in Fig. 2, and activation is achieved by treatment with orthophosphoric acid. The latter is a common activating agent used to prepare AC from agricultural by-products and works by promoting the bonding of volatile matter to the carbon material, thus increasing the carbon yield [93]. Characterization of the adsorbent surface by Scanning Electron Microscopy (SEM) revealed prominent, regular, and well-developed pores on the surface of the acid-activated bean husks relative to the uneven and irregular pores on the surface of the raw bean husks. Bello and co-authors noted a positive correlation between the adsorption capacity and the initial concentration of ibuprofen and temperature. The maximum adsorption capacity of 50 $mg.g^{-1}$ was recorded at 50 °C. The optimal reported pH for adsorption was 4.75, at which both ibuprofen and the bean husks are in their neutral forms. The high removal efficiency and regeneration potential of bean husks make them competitive sustainable adsorbents. However, the repeated use of acids for the activation (orthophosphoric acid) and regeneration (hydrochloric acid) of the bean husks increases their production cost and adverse impacts on the environment. Furthermore, experimental conditions should mimic, as closely as possible, real environmental conditions, especially when considering extrapolating the application to actual wastewater treatment. For instance, the optimal pH for the adsorption of ibuprofen at 4.75 does not intersect with the optimal pH encountered in wastewater treatment plants, where a narrow pH range is kept between 7 and 8. Bello and coworkers also derived AC from kola nut husks and conducted adsorption experiments on ibuprofen following close experimental conditions as with the functionalized bean husks. However, the major highlight in their study was the addition of a cost analysis section breaking down the cost required to produce 1 kg of adsorbent. Economic feasibility is one of the main pillars of sustainability assessment of green adsorbents and should be included in studies where novel adsorbents are introduced. The acid-modified kola nut husks were found to be six times cheaper as compared to conventional activated carbon [19], and thus demonstrate their cost-effectiveness. Furthermore, Nourmoradi and coworkers introduced AC derived from *Quercus Brantii* (Oak) to study the removal of ibuprofen. The resultant AC displayed a maximum adsorption capacity of 96.15 $mg.g^{-1}$ after a contact time of 120 min and at a pH of 3. The authors highlighted the role of using different chemical activators on the adsorption capacity. Multiple basic, acid, and salt activators were tested, including potassium and sodium peroxides, zinc, and ammonium chlorides, however, orthophosphoric acid preserved the highest sorption capacity among all [80]. Date stones are another type of agricultural waste that was tested [40]. The study estimates that a notable 90, 000 tons of AC can be produced with only 10% of the available date stone waste. The adsorbent was produced in a two-step process starting with the pyrolysis of the date stones into a char product, followed by the thermal treatment of orthophosphoric acid-impregnated chars at 550 °C for 2 h. The maximum adsorption capacity reached 126 $mg.g^{-1}$ at a pH of 7.

More recently, a single study evaluated six different ACs derived from multiple agricultural sources for the adsorption of ibuprofen, as well as other pharmaceutical products [94]. The ACs originated from red mombin seeds, external and internal parts of mango seeds, corn cobs, ice cream beans, and coffee husks, and were chemically activated using $ZnCl_2$ at 600 °C under a nitrogen atmosphere for 2 h. The adsorption of ibuprofen on the carbonaceous material was mainly via non-covalent interactions. These include van der Waals forces between the carboxyl group of ibuprofen and the carbonyl and phenol groups of the AC, in addition to the π-π interactions of the conjugated double carbon-carbon bonds of both ibuprofen and the ACs. Additionally, the large volume of the micropores as well as the high rate of graphitization showed a synergistic effect in enhancing the adsorption capacity of ibuprofen by the ACs.

Baccar and coauthors evaluated the removal of ibuprofen using olive-waste cakes. The adsorption was explored for ibuprofen as a single compound and ibuprofen in a mixture of pharmaceuticals, including ketoprofen and naproxen, in an attempt to examine the effect of competitive adsorption between the different pharmaceuticals [46]. The AC was produced using phosphoric acid as a chemical activator, followed by pyrolysis at 450 °C for 2 h. The maximum adsorption capacity determined from the Langmuir isotherm model is 10.83 $mg.g^{-1}$ at 25 °C for ibuprofen alone. However, a lower adsorption capacity was reported for ibuprofen from the mixture of the three pharmaceuticals. The pH of the medium had a strong influence on the adsorption process, which showed a decrease with increasing pH due to the electrostatic repulsion between the surface of the adsorbent and ibuprofen, both negatively charged at basic

pH. Moreover, the low adsorption was attributed to the aggregation of ibuprofen, which prevents the molecules from accessing the pores of the AC.

In parallel, extensive research is ongoing to find alternative low-cost sources for AC production from agricultural residues to remove carbamazepine. For instance, Sousa and coworkers invested in upcycled material from the brewing industry for the removal of carbamazepine [95]. Spent Brewery Grains (SBGs) represent around 85% of the waste generated by the brewing industry [96], which is estimated to be about 39 million tons per year [97]. From an environmental perspective, utilizing SBGs as potential adsorbents to remove pharmaceuticals from wastewater would add value to agro-industrial wastes, and minimize their disposal costs [95]. The authors tested several conditions to produce the adsorbent material. For instance, pyrolysis was conducted at two different temperatures of 600 and 800 °C, and two different residence times of 60 and 150 min. Moreover, several chemical activators were essayed, namely KOH, NaOH, and H_3PO_4. The authors opted for the Barley Wine (BW) and the Pilsener (PL) activated with KOH at 800 °C for 150 min, to produce KOH-BW-800-150 and KOH-PL-800-150, respectively. These were selected for further experiments, having the highest fixed carbon levels determined by proximate analysis, as well as the highest surface areas (1090 and 1120 $m^2.g^{-1}$), pore volumes (0.55 and 0.60 $cm^3.g^{-1}$), and micropore volumes (0.44 and 0.46 $cm^3.g^{-1}$). The selected adsorbents have also displayed the highest adsorptive capacity during preliminary testing. At a temperature of 25 °C and an initial concentration of carbamazepine of 5 $mg.L^{-1}$, the adsorption capacity for KOH-BW-800-150 was around 190 $mg.g^{-1}$ with a concentration of 15 $mg.L^{-1}$ of adsorbent, while that of KOH-PL-800-150 was around 178 $mg.g^{-1}$ with a concentration of 40 $mg.L^{-1}$ of adsorbent. Interestingly, both adsorbents were also applied to remove carbamazepine from real wastewater samples. The result was a decrease in the maximal adsorption capacity of approximately 70 and 60% for KOH-BW-800-150 and KOH-PL-800-150, respectively, as compared to the solutions prepared in ultrapure water. Sousa and coworkers attributed this to the potential interference of the complex components of organic and inorganic pollutants existing in wastewater. Regeneration experiments were not reported in this work; however, the high adsorption efficiencies and abundance of spent brewery grains favor their cost-efficient use as promising adsorbents for carbamazepine removal.

Additionally, Delgado and coworkers tested a powdered activated carbon of vegetable origins, and reported a significant maximal adsorption capacity of 242 $mg.g^{-1}$ [98]. Notably, an 85% removal efficiency was reported when experimenting at environmentally relevant levels of carbamazepine, offering promising prospects. Moreover, Torellas *et al.* synthesized activated carbons from peach stones using phosphoric acid as an activating agent and reported a maximum adsorption capacity of 335 $mg.g^{-1}$ [99]. The authors attributed the high adsorption to the hydrophobicity of carbamazepine.

3.3. Biochar

Agricultural waste also served as raw material for the production of biochar in multiple studies. Biochar is fine-grained charcoal, rich in inorganic carbon, and produced by the pyrolysis of naturally available biomass and plant wastes such as wood and fruit peels, in an oxygen-limited atmosphere [100,101,102]. Similarly to AC, the effectiveness of biochar as an adsorbent lies in its intrinsic physicochemical properties that hold a large surface area with a large pore size and volume, high stability, coupled with a high water-retaining capacity. Literature reports that the surface of biochar is naturally rich in functional groups, i.e., hydroxyl, carboxyl, and amine groups [14]. In addition, as is the case with many natural adsorbents, the biochar adsorptive properties can be further improved upon the functionalization of the surface [103]. However, the production of biochar does not require chemical nor physical activation, making the production process less costly than that of AC [104,105]. For instance, it was reported that producing one ton of biochar costs around 246$, making it six times cheaper than the 1500$ required to produce one ton of commercially AC [106].

Pepper stems were utilized to derive biochar using a one-stage pyrolysis process, and were explored as potential adsorbents for removing ibuprofen [14]. According to the Langmuir model, the produced biochar demonstrated exceptional removal capacity, reaching 569.6 mg of ibuprofen per gram of biochar. The adsorption process was mainly affected by the pH of the solution, which constantly alters the surface charges of both the biochar and ibuprofen. The ionic strength of the solution had less contribution to ibuprofen uptake by the biochar, minimizing the role of electrostatic interactions in the adsorption process. Biochar derived from mung bean husks also served as a potential adsorbent for ibuprofen in a study led by Mondal and co-authors [107]. The biochar derived from mung bean husks displayed a 99.16% removal efficiency under optimal conditions of 100 $mg.L^{-1}$ of adsorbent dose, 20 $mg.L^{-1}$ of initial ibuprofen concentration, a temperature of 20 °C, a pH of 2, and a contact time of 120 min to reach equilibrium. The maximum adsorption capacity was around 59.76 $mg.g^{-1}$ when the adsorbate concentration was 100 $mg.L^{-1}$. In their study, Mondal and co-authors emphasized the critical role of pH in determining the adsorption process between ibuprofen and mung bean husks. Indeed, changing the pH results in changing the overall charge of the adsorbent surface and ibuprofen, and governs the ensuing repulsive or attractive forces between them. The advantage of the production of biochar from mung bean husks is the application of a thermal activation process instead of acid activation, which reduces the negative environmental impact and the production costs of the adsorbent, thus increasing its environmental and economic sustainability. Moreover, the authors included a cost analysis and concluded that the production of biochar from mung bean husks remains a more cost-efficient alternative relative to commercial AC. However, data on the adsorbent regeneration were lacking, preventing firm conclusions on the overall sustainability of the adsorbent [107].

In line with the exploitation of natural material as potential adsorbents, and to further highlight the importance of activation in producing green adsorbents, Chakraborty *et al.* derived activated and non-activated biochar from the shells of a fruit, *Aegle marmelos*, also known as wood apple, to remove ibuprofen. The synthesis process involved carbonization at 650 °C for 1 h to produce wood apple biochar (WAB) and activation of the carbonized biochar under a superheated stream at 800 °C for 1.5 h to produce the steam-activated wood apple biochar (WASAB). A comparative study of the maximum capacity of both adsorbents to uptake ibuprofen from aqueous solutions displayed a removal of 5 and 12.658 $mg.g^{-1}$ for WAB and WASAB, respectively. Recovery of WAB and WASAB by methanol

desorption of ibuprofen from the doped adsorbents resulted in an efficiency decrease from 74 to 61% for WAB and from 81 to 69% for WASAB after four regeneration cycles. The study further assessed the performance of the adsorbents, WAB and WASAB, in removing ibuprofen from a mixture of pharmaceuticals. This mimics real environmental scenarios, as pharmaceuticals do not exist as single contaminants in aqueous matrices. Interestingly, the removal of ibuprofen decreased in the presence of diclofenac for both sorbents [108]. In the same context, Shin and coworkers invested in spent coffee wastes (SCWs) to derive pristine and activated biochar and examined the competitive adsorption of three pharmaceuticals including ibuprofen [71]. The biochar was activated with NaOH followed by pyrolysis at 800 °C for 2 h under a pure N_2 gas atmosphere. To increase environmental realism, the authors assessed the removal of pharmaceuticals in wastewater effluents and lake water in field-scale experiments. The reported removal of ibuprofen was 16.2 and 20.65 μmol.g^{-1} for the pristine biochar, corresponding to 3.34 and 4.26 mg.g^{-1} in lake water and wastewater effluents, respectively. Whereas the NaOH-activated SCW biochar increased ibuprofen removal to 80.02 μmol.g^{-1} and 61.25 μmol.g^{-1}, equivalent to 16.5 and 12.63 mg.g^{-1}, in lake water and wastewater effluents, respectively. However, no single compound experiments were conducted to allow the comparison of the adsorption behavior of ibuprofen alone relative to the mixture. Interestingly, the adsorption of ibuprofen on the pristine and the NaOH-activated biochar responded to different mechanisms, primarily moving from a multilayer to monolayer adsorption upon the activation of the biochar. Overall, the activation of the biochar improved its adsorptive performance. Yang and coauthors invested in plane tree leaves to produce plane tree leaf-derived biochar (P-BC) [109]. The production process is rather simple, the pre-treated leaves were subjected to pyrolysis at 600 °C for 2 h to produce P-BC, with a yield of 34.3%. Hydrogen bonding dominated the adsorption mechanism at low pH levels, increasing the pH resulted in a decreased adsorption efficiency mainly due to electrostatic repulsion between ibuprofen and the adsorbent, both negatively charged. The authors estimated the cost for producing 1 kg of biochar to be around 4.05$, and with the possible regeneration of the biochar for up to 5 cycles, preserving 70% of its efficiency, the environmental and economic practicality of the adsorbent seems promising.

Naghdi and coworkers used residues of pinewood to produce pinewood-derived nanobiochar. The low-cost and easily synthesized adsorbent was then applied for the removal of carbamazepine [110,24] which exhibited a 95% removal within the first 3 h of contact time. This was attributed to the fast mass transfer of the small-size particles of carbamazepine and the availability of vacant sites on the surface of the adsorbent [111,24]. Carbamazepine adsorption was enhanced by increasing the pH from 3 to 6; a further increase in the pH to a value of 8 did not cause any significant change in the removal efficiency. Increased efficiency from 53 to 87% was also reported with increased adsorbent dose from 200 to 1000 mg.L^{-1}. However, several studies report that a significant increase in the adsorbent dose may ultimately contribute to the decrease in the total number of available active sites for adsorption as a result of the overcrowding of the adsorbent particles and thus, their aggregation [112,113,111,24]. The work of Naghdi *et al.* indicated that carbamazepine removal through nanobiochar exhibited faster adsorption rates as compared to other carbonaceous materials such as AC, carbon nanotubes, and graphene oxide, probably due to the low tested concentrations of carbamazepine ranging between 0.5 and 20 μg.L^{-1}, simulating real contamination levels. Desorption experiments for adsorbent regeneration were not reported, and therefore the sustainability of this green adsorbent cannot be fully assessed.

3.4. Other adsorbents investigated for the removal of ibuprofen and carbamazepine

The potential of nano adsorbents has been considered for decontaminating water from pharmaceuticals. Nano adsorbents are particles ranging between 1 and 100 nm in size, they hold special physical and chemical characteristics such as high catalytic potential and reactivity [114,115], and their nano-sized structure offers them a higher ratio of surface area to particle size. Abdel-Aziz and co-authors successfully produced zero-valent Fe/Cu nanoparticles by green synthesis derived from *Ficus Benjamina* leaves and applied them for water purification from carbamazepine [116]. Based on the Langmuir isotherm model, the maximum adsorption capacity reached 26.15 mg.g^{-1}.

An interesting study was piloted by Kebede and coworkers to produce an adsorbent capable of removing carbamazepine and four NSAIDs (ketoprofen, fenoprofen, diclofenac, and ibuprofen), from wastewater by utilizing a protein extracted from *Moringa stenopetala* seeds [117]. *Moringa stenopetala* is a common tree in southern Ethiopia, which seeds have been widely used in water purification for their ability to coagulate impurities. Recently, tree seeds grabbed attention for their possible application as adsorbents in wastewater treatment. The adsorbent in the form of a protein powder is prepared through a series of steps detailed by Ndabigengesere and co-workers [118]. In their study, the authors reported a maximum adsorption capacity of around 32.12 mg.g^{-1} with an initial concentration of carbamazepine of 1 mg.L^{-1}, an adsorbent dose of 4 mg.L^{-1}, a temperature of 23 °C, and a pH of 3.25. The water-soluble protein was positively charged at acidic pH, as a result of the protonation of its amide and amine functional groups. The adsorbent surface was zwitterionic at pH values between 5 and 10 and became predominantly negative at a pH above 10. The adsorption mechanism was therefore assumed to be controlled by the amine, amide, and alcohol functional groups of the protein adsorbent. Interestingly, Kebede *et al.* applied the adsorbent to real wastewater samples and reported 86% removal of carbamazepine as compared to 100% removal in a synthetic standard mixture solution. The proteins extracted from *Moringa Stenopetala* seeds are therefore promising material that can be applied for the removal of carbamazepine, being a simple, environmentally friendly, and cost-effective adsorbent.

3.5. Summary

The reviewed literature on the use of green adsorbents for ibuprofen removal from aquatic media is summarized in Table 2.

The reported adsorption capacities for the reviewed adsorbents originating from agricultural wastes range between 5 and 569.6 mg.g^{-1}. Other green adsorbents were also derived from multiple sources and explored for the same purpose. For instance, Liu and

coauthors synthesized a genipin-crosslinked chitosan/graphene oxide-SO_3H composite (GC/MGO-SO_3H) and reported an adsorption capacity of 138.12 mg.g^{-1} [119]. Genipin is a water-soluble bi-functional crosslinking reagent isolated from gardenia fruits [120], and chitosan is a semisynthetic compound extracted and derived from the deacetylation of chitin, a naturally occurring product of crustaceans' waste, squid, and oyster [121,122,123]. Although chitosan is widely applied in the wastewater treatment field as a bio-adsorbent [124], it exhibits several limitations such as low hydrophilicity and porosity, which explains the need for modification to improve its adsorption capacity. Żółtowska *et al.* also synthesized an adsorbent derived from chitin, originating from crab shells. Chitin was mixed with kraft lignin [125], a biopolymer obtained from kraft pulp [126], to create the modified adsorbent and enhance its efficiency with the rich functional groups carried by lignin, i.e., alcohol hydroxyl, phenolic hydroxyl, carbonyl, carboxyl, methoxyl, and sulfonic acid [127]. Despite the use of kraft lignin to enhance the adsorption capacity of chitin, the maximum measured adsorption capacity was in the order of 0.26 mg.g^{-1}, a value considered to be low as compared to the sorption capacities of the other adsorbents [125]. The drawback of applying chitosan-based adsorbents is their biodegradability which limits their continuous regeneration [128]. However, biodegradability renders the disposal of the spent adsorbent more accessible.

Furthermore, novel synthetic adsorbents are continuously introduced and evaluated for the removal of ibuprofen. The lowest and highest reported adsorption capacities were 66.67 μg.g^{-1} and 320 mg.g^{-1} for composite iron nanosorbents [62] and MOFs derived from porous carbon [60], respectively. MOFs are a class of hybrid adsorption material constructed by the integration of inorganic metals with organic linkers in a 3D crystalline network; using different particle shapes and different organic and inorganic combinations results in different MOFs [129,130]. The adsorbents exhibit a high porosity and surface area structure that can be further

Table 2
Summary of the literature on the use of agro-waste-based adsorbents for ibuprofen removal.

Adsorbent	Adsorbent Concentration	Ibuprofen Concentration	Contact Time	pH/ Temperature	Adsorption Capacity	Sorbent Reuse/ Regeneration Cycles/ Efficiency	References
Crushed Knotweed	5000 mg.L^{-1}	100 mg.L^{-1}	6 h	NA 293 K	38.2 mg.g^{-1}	NA	[73]
Cocoa-shell	500 mg.L^{-1}	30 mg.L^{-1}	90–120 min	2 295	23.18 mg.g^{-1}	NA	[74]
Functionalized cocoa-shell	500 mg.L^{-1}	30 mg.L^{-1}	90–120 min	2 295	26.98 mg.g^{-1}	NA	[74]
Acid-activated bean husks	2000 mg.L^{-1}	50 mg.L^{-1}	40 min	4.75 313 K	24.57 mg.g^{-1}	NA 94.68%	[92]
Acid-modified Kola Nut Husks	100 mg.L^{-1}	50 mg.L^{-1}	180 min	NA 303 K	24.161 mg.g^{-1}	4 cycles 97%	[19]
Steam-activated mung bean husk biochar	100 mg.L^{-1}	20 mg.L^{-1}	120 min	2 298 K	59.76 mg.g^{-1}	NA	[107]
AC derived from *Quercus Brantii*	1000 mg.L^{-1}	100 mg.L^{-1}	120 min	7 298 K	35.49 mg.g^{-1}	NA	[80]
Pepper Stems (PS) biochar	1000 mg.L^{-1}	NA	240 min	7 293 K	569.6 mg.g^{-1}	4 cycles 46.07%	[14]
Moringa stenopetala seeds	4000 mg.L^{-1}	1 mg.L^{-1}	NA	3.25 296 K	16.67 mg.g^{-1}	NA	[117]
Wood Apple Biochar (WAB)	330 mg.L^{-1}	15 mg.L^{-1}	22 h	3 288 K	5 mg g^{-1}	4 cycles 61%	[108]
Wood Apple Steam Activated Biochar (WASAB)	1000 mg.L^{-1}	30 mg.L^{-1}	16 h	2 293 K	12.658 mg.g^{-1}	4 cycles 69%	[108]
Pristine SCW biochar	150 mg.L^{-1}	6.18 mg.L^{-1}	24 h	7 298 K	3.34 mg.g^{-1} 4.26 mg.g^{-1}	NA	[71]
NaOH-activated SCW biochar	150 mg.L^{-1}	6.18 mg.L^{-1}	24 h	7 298 K	16.50 mg.g^{-1} 12.63 mg.g^{-1}	NA	[71]
Plane tree leaf-derived biochar	1000 mg.L^{-1}	2 mg.L^{-1}	NA	2 NA	10.41 mg.g^{-1}	5 cycles 70%	[109]
Red Mombin Seeds	500 mg.L^{-1}	50 mg.L^{-1}	120 min	4–5 296 K	181.62 mg.g^{-1}	NA	[94]
Internal parts of Mango seeds	500 mg.L^{-1}	50 mg.L^{-1}	120 min	4–5 296 K	130.05 mg.g^{-1}	NA	[94]
External parts of Mango Seeds	500 mg.L^{-1}	50 mg.L^{-1}	120 min	4–5 296 K	169.49 mg.g^{-1}	NA	[94]
Corn cobs	500 mg.L^{-1}	50 mg.L^{-1}	120 min	4–5 296 K	158.99 mg.g^{-1}	NA	[94]
Ice cream beans	500 mg.L^{-1}	50 mg.L^{-1}	120 min	4–5 296 K	108.56 mg.g^{-1}	NA	[94]
Coffee husks	500 mg.L^{-1}	50 mg.L^{-1}	120 min	4–5 296 K	129.2 mg.g^{-1}	NA	[94]
Waste Date stones	50 mg.L^{-1}	1 mg.L^{-1}	24 h	7 293 K	126 mg.g^{-1}	NA	[40]
Olive-waste cakes	NA	10.4 mg.L^{-1}	26 h	4.12 298 K	10.83 mg.g^{-1}	NA	[46]

adjusted to meet selective applications by changing the metals, the organic ligands, and the introduced functional groups.

Table 3 summarizes the reviewed literature on the removal of carbamazepine using agro-waste adsorbents.

The reported adsorption capacities for carbamazepine using agro-waste-based adsorbents range between 74 μg.g^{-1} and 335 mg.g^{-1}. Additionally, many studies invested in other sources to produce green adsorbents, namely industrial waste consisting of sludge originating from paper mill production [79]. The amount of waste produced by this industry is estimated to be around 11 million tons by the European pulp and paper industry alone [131]. The maximum adsorption capacity of the adsorbent was around 24 mg.g^{-1} and 10 mg.g^{-1} in ultrapure water and wastewater, respectively. Interestingly, the study compared the performance of the produced adsorbent with the commercially available granular AC, the latter had a significantly higher adsorption capacity reaching 85 mg.g^{-1} in ultrapure water. Similarly, Calisto and coauthors produced a non-activated carbon by pyrolysis of primary paper mill sludge (PS800-150) and compared the results to commercially available AC (PBFG4) [132]. The results were in accordance with the previous study, where the reported maximum adsorption capacities were higher for the commercial AC (116 mg.g^{-1}) as compared to PS800-150 (12.6 mg.g^{-1}).

Moreover, multiple synthetic adsorbents were evaluated for their potential in removing carbamazepine. Indeed, carbon nanotubes have been recently attracting significant research interest thanks to their exceptional physical and chemical properties [133]. Deng and co-authors synthesized carbon-dot and magnetite-modified carbon nanotubes CMNTs intending to evaluate their use as an adsorbent for the removal of carbamazepine [22]. The adsorption capacity was determined at 65 mg.g^{-1} with an initial concentration of 20 mg.L^{-1} of carbamazepine, 200 mg.L^{-1} of adsorbent, a temperature of 298 K, and a pH of 7. Another study evaluated the removal of carbamazepine from water samples using hematite nanoparticles [23], which is an iron-oxide nanoparticle that is extremely stable and carries magnetic properties [134]. Chemical-based synthesis of these particles has proven to be expensive and to require special equipment, which is why Rajendran and coworkers used the bacterial strain *Bacillus cereus* SVK1 as a microorganism for the biosynthesis of hematite, as proposed by Riddin *et al.* [135]. The result was a spherical nanoparticle of size ranging between 14 and 50 nm with a maximum adsorption capacity of carbamazepine reaching 2.89 mg.g^{-1}.

4. Adsorption isotherms and kinetics

The adsorption isotherm equations allow the determination of the equilibrium performance at a constant temperature [136], as well as the mechanism of interaction between the adsorbent and adsorbate [137]. The Langmuir and Freundlich isotherm models were the most frequently used to fit the experimental data obtained from the adsorption of ibuprofen and carbamazepine. The Langmuir model basically assumes an entirely monolayer adsorption, and the absence of interaction between adsorbate species. The linearized model of the Langmuir isotherm is expressed by Eq. (1)

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{1}$$

Where $\boldsymbol{Q_m}$ represents the maximum monolayer adsorption capacity of the adsorbent (mg.g^{-1}), and $\boldsymbol{K_L}$ represents the Langmuir equilibrium constant (L.mg^{-1}) describing the affinity between the adsorbent and adsorbate [137,138]. The Freundlich isotherm model describes a multilayer adsorption with interaction between the adsorbed molecules [137], and assumes a heterogeneous surface with a non-uniform distribution of the heat of adsorption [139]. The model, however, does not assess the adsorption behavior of the adsorbent at saturation [138]. The linear form of the Freundlich isotherm can be described by Eq. (2)

$$log\ q_e = log\ K_f + \frac{1}{n}\ log\ C_e \tag{2}$$

Table 3
Summary of the literature on the use of agro-waste-based adsorbents for the removal of carbamazepine.

Adsorbent	Adsorbent Concentration	Carbamazepine Concentration	Contact Time	pH Temperature	Adsorption Capacity	Reuse/Regeneration Cycles/Efficiency	References
Rice straws	1000.mg L^{-1}	100.mg L^{-1}	120 min	6.8 301 K	4.01 mg.g^{-1}	NA	[75]
Pinewood derived nanobiochar	100 mg.L^{-1}	NA	4 days	6 298 K	~74 μg.g^{-1}	NA	[24]
Moringa stenopetala seeds	4000 mg.L^{-1}	1 mg.L^{-1}	NA	3.25 296 K	32.12 mg.g^{-1}	NA	[117]
KOH-BW-800-150	15 mg.L^{-1}	5 mg.L^{-1}	120–240 min	7 298 K	190 mg.g^{-1}	NA	[95]
KOH-PL-800-150	40 mg.L^{-1}	5 mg.L^{-1}	120–240 min	7 298 K	178 mg.g^{-1}	NA	[95]
AC of vegetable origin	100 mg.L^{-1}	10 mg.L^{-1}	72 h	NA 298 K	242 mg.g^{-1}	NA	[98]
AC derived from peach stones	2400 mg.L^{-1}	100 mg.L^{-1}	NA	NA 303 K	335 mg.g^{-1}	NA	[99]
Green synthesis zero-valent Iron/Cu nanoparticles	200 mg.L^{-1}	5 mg.L^{-1}	20 min	5 293 K	26.15 mg.g^{-1}	NA	[116]

Where K_F corresponds to the adsorption capacity $(mg.g^{-1})/(mg.L^{-1})^n$ and n corresponds to the adsorption intensity (dimensionless). The inverse of n is an indicator used to assess the favorability of the adsorption [137]. According to the Freundlich isotherm, the adsorption is linear for a value of n equal to 1, favorable for values above 1, and unfavorable for values less than 1 [138]. Most commonly, the experimental data from the adsorption of ibuprofen and carbamazepine fitted the Langmuir isotherm model.

Adsorption kinetics investigate the effect of contact time on the adsorption process and determine the rate at which adsorption occurs. In most of the reviewed literature, the experimental kinetic data were fitted to two main kinetic models, namely, the linear forms of the pseudo-first order (PFO) and pseudo-second order (PSO) models. These are respectively expressed by Eq. (3) and Eq. (4)

$$ln(q_e - q_t) = ln\, q_e - k_1.t \tag{3}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{4}$$

Where q_e and q_t $(mg.g^{-1})$ represent the amounts of adsorbate adsorbed at equilibrium and at time t, respectively. T represents the adsorption time (min), k_1 and k_2 (min^{-1}) represent the pseudo-first and pseudo-second-order adsorption rate constants, respectively [140]. The pseudo-second order model was the most frequently encountered kinetic model across studies, which assumes a proportionality between the rate of adsorption and the vacant adsorbent active sites [44].

5. Regeneration and disposal of spent adsorbents

The recovery and sustainable management of spent adsorbents is a major challenge when attempting to close the life cycle analysis of the adsorbent. Practically, spent adsorbents can be separated from treated water effluents through filtration or magnetic separation, among other techniques. Adsorbents are then either disposed of or regenerated for further use. Estimates of the treatment cost of adsorbent residues, including dewatering, transport, and treatment by incineration or landfilling are around 100€ per ton [141]. A general disregard is noted across studies toward the final disposal of the adsorbents after exhaustion. Spent adsorbents concentrating contaminants require treatment as hazardous wastes [142], or must undergo desorption before disposal.

Selecting a proper regeneration technique is crucial in determining the desorption efficiency and the stability of the recycled adsorbent. Many techniques explore the possibility of adsorbent regeneration without separating it from the liquid matrix. Microbial-assisted adsorbent regeneration allows microbial degradation of the adsorbed contaminant during biological wastewater treatment. However, some adsorbates may exhibit toxic effects on the biodegrading microbes and disrupt the treatment process. Moreover, the biodegradability of organic adsorbents can be a major limitation for their use in contaminants removal as their stability is compromised after exposure to some microbial populations that may induce their biological degradation, and consequently alter the adsorption process. Conversely, the biodegradable nature of green organic adsorbents can alleviate the burden of their disposal after their complete exhaustion and makes them sustainable alternatives to synthetic non-biodegradable adsorbents [2,143,144,145]. Eventually, predicting the behavior of green adsorbents is crucial, particularly when large-scale practical applications are considered.

6. Limitations and future considerations

Despite the many high grounds offered by adsorption methods, their use in the removal of pharmaceuticals from aqueous media is associated with some limitations and drawbacks. Adsorption is a nondestructive technique involving only a transfer of contaminants and therefore imposes ulterior problems of sludge disposal. On another level, pharmaceuticals subsist in aqueous media as mixtures where possible competition or interference from organic and inorganic pollutants occurs, unlike the conditions in prepared standard solutions or ultrapure water. This highlights the importance of reproducing environmental conditions in bench-scale adsorption experiments for increased environmental realism and confidence in extrapolating laboratory results to the field scale. Furthermore, a single adsorbent is not able to interact with and remove all the complex mixtures of pharmaceuticals given their diverse chemical structures. Therefore, it is crucial to understand the chemical structures of both adsorbents and adsorbates and how it affects the mechanisms of their interaction, which ought to be considered when engineering and tuning adsorbents for enhanced removal of contaminants. Given so, monitoring should necessarily be implemented to deliver accurate knowledge on the existing levels of contamination, and further research on toxicity and health effects of pharmaceutical pollutants ought to be conducted to determine the candidates for routine monitoring. Still and all, focusing only on end-of-pipe green technologies for water treatment is not sufficiently sustainable and prevention remains the ultimate technique. As such, proper strategies to reduce the input of pharmaceuticals into the environment is the first step towards a sustainable environment. Moreover, a holistic green approach encompassing the full life cycle of pharmaceuticals from manufacturing to disposal offers a well-grounded, environmentally friendly passageway that ensures sustainable pharmaceutical production and mitigates their risks on the environment [19,146].

7. Conclusion

This literature review focused on the removal of two highly occurring pharmaceuticals in the environment, ibuprofen, and carbamazepine, through the application of agro-waste-based green adsorbents. Novel adsorbents are constantly being produced to enhance the removal of pharmaceuticals from contaminated waters at reduced cost and time and with minimal use of the adsorbent material, thus ensuring high efficiency and sustainability of the process. For this aim, waste-based carbons produced from the

upcycling of residual agro-wastes are recently gaining interest as potentially sustainable alternatives to commercially available adsorbents. The reviewed studies reveal the existence of a multitude of efficient green adsorbents which could be used for the removal of ibuprofen and carbamazepine from contaminated waters. However, comparing the efficiencies of adsorbents across studies is not a straightforward process and is a rather complex task. The reported adsorption data does not allow us to favor one type of the adsorbents over another nor to come to ultimate conclusions in view of the fact that the comparison must simultaneously account for the production steps, the overall adsorbent yield, and ultimately the experimental conditions, mainly the pH and the temperature. This is especially relevant when considering that the high adsorption capacity is limited to acidic/basic pH and/or environmentally irrelevant temperatures which restrict the application of the adsorbent to laboratory-scale batch experiments. The combined effect of multiple influencing parameters needs to be considered prior to upscaling their use to wastewater treatment plants.

Ideally, the best adsorbent should meet multiple requirements, among which are cost-efficiency, chemical and mechanical integrity, high adsorption capacity, and the aptitude of being regenerated [147], and safely disposed of. Owing to the natural availability of the raw material, the cost-efficiency and environmental friendliness of green agro-waste-based adsorbents remain unarguable as compared to synthetic adsorbents. However, the lack of regeneration studies makes it more difficult to conclude on the sustainability of the tested adsorbents. Moreover, enhancing the efficiency of green adsorbents, which is commonly reported by post-production surface modification and functionalization of the natural adsorbent, entails drawbacks on the environment since most activators are acid or alkali-based.

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Declaration of competing interest

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

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