

Lignocellulosic-Based Sorbents: A Review

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Biosorbents are usually used in raw or processed forms such as activated carbon (AC), biobar (BC), and charcoal (CC) for removal of pharmaceuticals, pesticides, organics, inorganics, mycotoxins, etc. from aqueous systems. Besides classical sorption of the pollutants, biosorbents have prospect of applications as electrodes in the microbial fuel cells, green packaging materials, energy storage devices, catalysts, soil remediation agent, carbon sequestration, etc. Hence, further concerted investigations should be exercised to develop feasibly best conditions for the preparations and modifications of biosorbents.

Keywords: lignocellulosic biomass ; biosorbent ; activation ; pollutants

1. Biosorbent

The combustion of fossil fuels is intensifying global warming and destructing ecosystem with negative human health impacts as well. As a result of these environmental challenges and decrease in fossil fuel feedstock, the need and use of biomass or renewable materials have become increasingly popular ^{[1][2][3][4]}. Lignocellulosic biomass is abundant and is an alternative renewable resource to traditional fossil chemicals. In addition, there is continuous search at the moment for new sustainable products with amenable properties ^{[5][6]}. Meanwhile, infiltration of the environment with heavy metals, radionuclides, organic pollutants, and mycotoxins with their impact on the ecosystem are of serious potential danger for all ^[7]. Means of getting rid of metal ions as a case in point include physical, chemical, and biological technologies ^{[8][9]}. However, the challenges of these technologies in pollutant treatment include, among others, copious sludge generation, safety problems, high cost, and lack of expertise ^{[7][10]}. Meanwhile, nowadays, the use of biosorption for pollutants cleaning is being paid much attention because of some inherent benefits ^{[11][12]} with much potential. In biosorption, ions or molecules are removed from aqueous phase by biomolecules, biomass (also lignocellulosic biomass), or its derivatives ^{[13][14][15]}. In addition, low cost, rapid regeneration, and easy access of biomass make them expediently promising precursors for the production biosorbents ^{[16][17]}. Thus, the advantages of biosorption include the use of renewable feedstocks ^{[18][19]} readily available, decrease in chemical or biological waste, high chances of biosorbents and metal recovery, and so on ^{[21][20]}. Therefore, we report the potentials of biosorbents and some related applications of these emerging biomaterials.

2. Adsorption Process

Adsorption may be considered as accumulation of adsorbate at the liquid-solid interface or gas-solid interface. There are two kinds of adsorption: chemical adsorption (chemisorption) and physical adsorption (physisorption) ^{[21][22]}. Physical adsorption, also known as physisorption, occurs when the attractive forces present between adsorbate and adsorbent are weak, like Van der Waals forces. It has low enthalpy of adsorption (i.e., ΔH adsorption = 20 to 40 KJ/mol) and occurs with development of multilayer of adsorbate on adsorbent. This phenomenon decreases with an increase in temperature and usually takes place at a lower temperature much below the boiling point of the adsorbate ^{[22][23]}. While chemical adsorption (chemisorption) takes place when the attractive forces between the adsorbate and adsorbent are chemical forces of attraction. Here, only a single layer formation of the adsorbate on adsorbent takes place and it has a high enthalpy of adsorption (i.e., ΔH adsorption = 200 to 400 KJ/mol). This phenomenon first increases and then decreases with a rise in temperature ^{[22][24]}. Often, most adsorption processes are controlled by physical forces ^{[21][22]}. More so, the adsorbate could be regenerated from the sorbent's surface. Usually, the rate of adsorption increases with increase in adsorbent dosage and vice versa, and rate of adsorption can be high if contact time is long and vice versa. More so, high rate of adsorption is found if adsorbate concentration is low and vice versa. Then, low rate of adsorption is obtained when pH is low and vice versa. Furthermore, low rate of adsorption is obtained if the temperature is too low or too high ^{[21][22]}. Thus, the possible mechanism routes of biosorption process are given in [Figure 1](#).

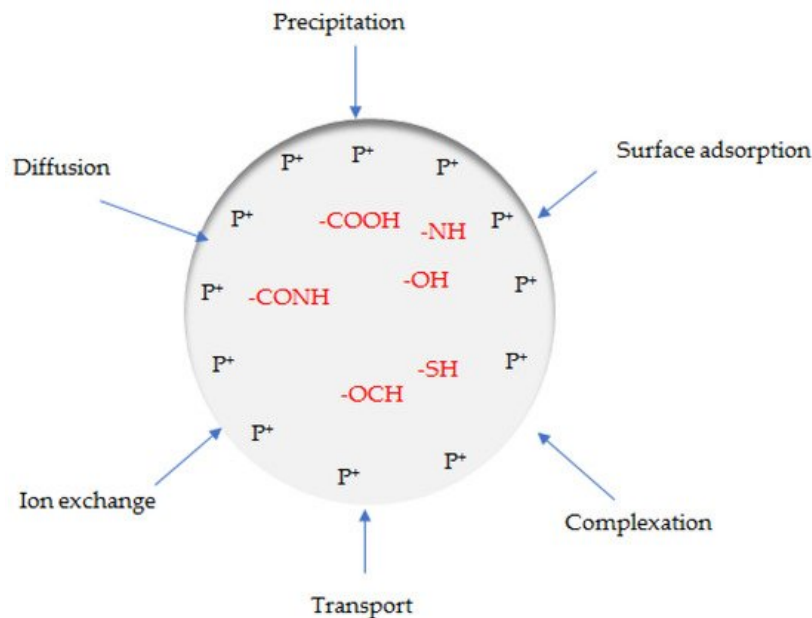


Figure 1. Possible mechanism routes for biosorbents (P^+ = pollutant and COOH, NH, OH, COH, SH, or OCH = functional groups).

3. Preparation of Sorbents from Lignocellulosic Biomass

Chemical, biological, and thermochemical processes are used for the conversion of biomass into sorbents. However, the thermochemical approach is often preferred because of faster processing duration, higher product, employment of entire biomass, and energy proficiency [18][25]. Hence, charcoal (CC), biochar (BC), and activated carbon (AC) are pyrogenic carbonaceous material (PCM) often derived from biomass [20][25][26][27][28][29][30][31]. In addition, sorbents could be prepared directly or by using catalyst/template [16]. For instance, preparation of hydrochar entails application of hydrothermal carbonisation (HTC). HTC involves the use of water for the transformation of biomass at about 100–350 °C to form hydrochar [18]. The traditional HTC synthesis of carbon materials is affected under harsh conditions. The improved HTC has become a more promising route since it holds potential of begetting high carbon efficiency and abundant functional groups on the product surface. Further, the rediscovered solvothermal approach of elevated pressure HTC and the thermocatalytic mild temperature conversion (LTC) process at atmospheric pressure have become important in the carbonisation process [32]. Furthermore, production of porous carbon material in one-pot step in an ionic liquids (ILs) medium without any support is achievable under the ionothermal carbonisation method of [18]. More so, gentle heating rate pyrolysis of biomass at about 400 °C can produce high amount of BC that enhances the soil fertility, cation-exchange, etc. On the other hand, if the pyrolysis is performed at higher temperatures (550–600 °C), lower amounts of BC is produced. The BC is high in aromatic carbon, microporosity, and alkalinity [18], but very low porosity and surface area [3]. However, this characteristic can be enhanced by physical activation [3]. In brief, preparations of biosorbents involve carbonization and activation processes. Carbonisation at elevated temperature under inert condition produces BC by removing the volatile matter through degradation [20][33][34][35]. The four stages of the carbonisation are: (a) moisture-drying at ≤ 200 °C; (b) at 170–300 °C there is formation of methanol and acetic acid, tars, then CO and CO₂; (c) production of biochar as pyrolygneous liquids and light tars are removed at 250–300 °C; and (d) at >300 °C; there is expulsion of volatile and noncarbon species to enhance carbon content of the biochar [20][36]. It is useful that suitable biomass with strong reproducibility and process methods be selected to enable efficient preparation of sorbent [20][37]. In addition, for efficient use and sustainability enhancement, biosorbent can be recycled after use so as to avoid littering and possible pollution.

3.1. Activation Process

Sorption capacity can be improved by increasing the surface area through direct activation or by activation after pyrolysis [38]. Activation is aimed at producing more active and functional sorbents [1][39][40]. Hence, biosorbents are activated so as to remove adsorbed unwanted materials [40][41][42][43], and to make functional groups become available for sorption [44][45][46][47]. Thermal activation has been known to be quite effective in forming strong sorbents [48][49][50][51]. More so, modification may be carried out on biosorbents in order to introduce non-carbon moieties to surface as to increase their sorption capacity [25][52]. We can choose to carry out modification after or instead of activation [25]. For physical activation, steam/pyrolysis/plasma heating is involved with activating agents such as nitrogen and carbon dioxide [1]. Further, in physical activation the impregnation of chemicals may be used along carbonisation (100–1000 °C as the case may be). Thus, these are some reported physical activation processes: carbonisation/impregnation of KOH [53][54], steam/N₂ [55][56]

[57], CO₂ [58][59][60], carbonisation only [61][62], and pyrolysis [63][64]. Since there is release of volatile basic compounds during the pyrolysis, the surface acidity is increased [61]. In general, for dual step process of physical activation, the precursor of the sorbent is carbonised at 400–700 °C, followed by activation with steam, air, or CO₂ [65]. On the other hand, for single-step process, carbonisation and activation take place concurrently at 600–800 °C [66]. In another way, biosorbent can be chemically activated with the means of hydrogen peroxide, zinc chloride, phosphoric acid, potassium hydroxide, nitric acid, sulphuric acid, hydrochloric acid, sodium hydroxide, steam, potassium carbonate, etc. [1]. The activating agents may be combined in the course of this: zinc chloride and nitric acid; phosphoric acid and nitric acid; hydrochloric acid and zinc chloride; sulphuric acid and sodium hydroxide; sulphuric acid and ammonium thiosulphate; succinic acid and sodium bicarbonate, and so on [1]. The highly active surface and presence or absence of groups like acidic hydroxyl, carbonyl, etc. can stimulate the uptake capacity of sorbents [55][67]. Now for a single-stage process of chemical activation, the material is subjected to dehydrating agents like H₃PO₄, ZnCl₂, KOH, and NaOH [68]. Otherwise, the stuff is carbonised to form biosorbent at 400–600 °C before chemical activation, known as the dual-stage process [69]. Further, we have another activation involving physical and chemical processes. Several literature have demonstrated such activation processes [1][36][53][57][70][71]. Oftentimes, physicochemical activation entails chemical addition before carbonization, or carbonisation prior to the chemical addition [72][73]. However, because Zn has been prohibitively classified as toxic heavy metal, its use in biomass activation has recently decreased. More so, its readiness of leaching into water [1] is a concern too. It is being found that physiochemical activation results in more pore structure and larger surface area. Lastly, microwave activation has also been recently used to produce sorbents. Thus, we can take advantage of the fact that this process is fast, has delocalised heating, is specific, clean, and has ease of regulation [69][71][74]. These different activation processes have similar potentials. The critical thing is the condition of the activation and perhaps the precursor used.

3.2. Some Characteristics of Biosorbents

Good biosorbents are supposed to have efficient surface area and porosity properties. They should also have high regenerability [1][25][49]. Hence, the adsorption capacity is function of the surface area, total porosity, and the surface chemistry [1]. For biosorbents to be deployed as a commercial grade, the surface area should be ≥ 500 m²/g [1]. Furthermore, smaller biosorbent particles have shorter path for diffusion, increased total surface area, and higher micro pore volume. This will in turn enhance the sorption power of the sorbent than those with bigger particles [75][76]. Sorbents with larger particles will have longer path for diffusion and lower active sites causing poor adsorption [77]. Appropriate surface area, porosity, particle, and functional groups on biosorbent make them suitable for decontamination of soils and water laden with heavy metals and organic compounds [78]. Furthermore, affinity to particular elements can facilitate its preferential uptake capacity as it was found for phenol adsorption in the presence of nitrogen [79]. The presence of π -electron donor/acceptor moieties in adsorbents can increase adsorption efficiency [80]. Additionally, high amount of ash in biosorbent favours adsorption of polar organic compounds [80].

3.3. Activated Carbon

AC is a carbonaceous material that is amorphous with high internal surface area and porosity [1]. It is produced from carbon source and amended to be used as sorbent of contaminants from gases and liquids [25][81][82][83]. Generally, the common sources of ACs are petroleum coke, lignite, bone char, peat, natural or synthetic polymers wood, coal, and other biomasses [1]. Raw material to be used for ACs production should be cheap, abundant, highly carbonaceous, and have low amount of ash, sulphur, and other impurities such as chloride and heavy metals [1]. Therefore, continuous need for energy storing device, potable water, environmental technologies are increasing the general demand for nascent ACs [84]. ACs are commonly applied for the treatment of wastewaters and emissions [1]. More recently, bioderived ACs are much desired because they are more sustainable, low-cost, high in carbon content, low in inorganic content, etc. [1][85]. More so, with the increasing amount of biomass waste generation, it is necessary to study the conversion of such waste to value-added products such adsorbents for removal of pollutants from wastewater. Therefore, olive stones activated carbons (OSACs) have been used in the removals of phenol (635 mg/g), iodine (1495 mg/g), nitrophenol, chlorophenol, ethanol, methylene blue (667 mg/g), Pb (148 mg/g), remazol red B, amoxicillin, safranin, and cadmium (200 mg/g) from wastewaters [1]. Chowdhury et al. [36] has also found that biosorbent from lignocellulosic biomass have demonstrated excellent capabilities for the removal of contaminants from waste aqueous stream [36]. Thus, ACs are effective in wastewater treatment by adsorption of the organics and inorganics [1]. Besides sorption, bioderived ACs can find use as catalysts [2][18][86][87] for anaerobic reduction and in the production radicals to oxidise pollutants of effluents [88][89]. They are also used in microbial fuel cells as electrodes [25][89][90]. Furthermore, these materials have demonstrated very efficient and superior capabilities for the esterification of diacids in aqueous solution than the commercial analogues [91][92].

3.4. Biochar

Biochar is an alternative to AC for decontamination of pollutants from environment [80][93]. BC can be sustainably produced from organic and agricultural wastes biomass feedstocks, sewage sludge, and forest residue [78][94]. Due to blockage of pores, BC obtained by carbonisation has a surface area of <300 m²/g [73]. However, these locked pores can be removed by activation [95] as earlier highlighted. Unlike ACs, BCs are produced from more diverse feedstocks in a less energy-intensive thermal conditions [25][96]. Thus, BC's surface area and mechanical hardness are often lower than ACs. There are increasing applications of BC in waste-water treatment [97][98]. Principally, sorption tendency/properties of BCs have resulted into many related applications. Hence, biochar acts as fertilizer [25][99][100][101][102][103], soil remediation agent [104] (like ACs [105][106]), and carbon sequestration [18][25][107][108][109][110]. Additionally, biochar is used in making green packaging materials for fruits and vegetables [106]. Recently, biochar is also used for amendment in concrete [111][112] and to enhance toughness capability of cement-based composites [5]. Applications of BC and AC are also overlapping in their recent times [25]. Activated carbon can be taken as BC if the AC is not withdrawn after use, or it was produced from renewable materials similar as BC [25][113]. However, the use of BC can affect efficacy of pesticides, soil organisms, and half-lives of organics and some sediments [78].

3.5. Charcoal

Charcoal (CC) is a carbonised wood used as fuel or reductant [114][115]. CC can be formed when BC is burned as a fuel [25]. About 70% production of charcoal is located in Africa [116][117][118] and used as domestic fuel or exported. Thus, CC can be used for making barbeques [119], metallurgy [120], sodium cyanide, carbon disulfide, or silicon, etc. [25]. Charcoal can be produced industrially using state-of-the-art facility [25]. Usually, traditional means such as earth mounds are used for the production of CC. There are environmental health issues because of emissions of VOCs, carbon monoxide, methane, and fine particulate matter [25][120][121]. The highlight and demonstration of lignocellulosic materials sorbents is given in Table 1 and Figure 2.

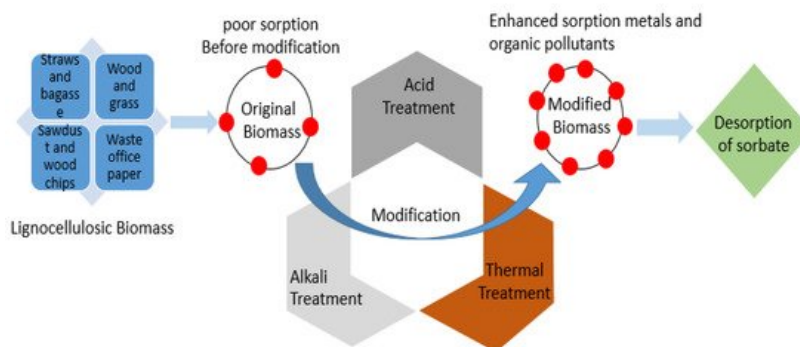


Figure 2. Illustration of use of biosorbents in removal of pollutants.

Table 1. Highlight of sorption capacity of some Biosorbents.

Adsorbate	Adsorbent (Adsorption Capacity, mg/g)	Ref. Respectively
Safranin	Olive stone (526); <i>Spirulina sp.</i> Algae (54);	[122][123]
Bisphenol A	Olive stone (2.7); <i>Ulva prolifera</i> (9);	[124][125]
Cadmium	Olive stone (200); <i>Diplotaxis harra</i> (32); <i>Glebionis coronaria</i> (58); <i>Solanum elaeagnifolium</i> (18.9)	[71][126][127][128]
Copper	Olive stone (34); Orange peel (9); Sugarcane bagasse (13); Coffee residues (70); Corn cob (31.35); Sal bark (51.4); mango (42.6); Jackfruit (17.4); Peanut shell (25.39); Papaya Seeds (212)	[22][129][130][131][132]
Lead	Olive stone (149); <i>Moringa oleifera</i> (12.24); <i>Solanum elaeagnifolium</i> (20.6); Banana Peel (7.97)	[22][128][133][134]
Nickel	Olive stone (24), Brown algae (64), Green algae (92); Waste black tea (90.91); <i>Solanum elaeagnifolium</i> (6.5)	[128][133][135]
Methylene blue dye	Olive stone (667); Bamboo (454); Fox nutshell (968); Biochar (114); Milled biochar (354); Banana peels (109.89)	[136][137][138][139][140][141]
Chromium	Olive stone (7); <i>Alga Pterocladia</i> (66); Biochar (21); Rice husk (16.94); saw dust (4.56); Coffee residues (45); Green tea leaves (99%); Peanut shell (27.86)	[22][142][132][143][144][145][146]

Adsorbate	Adsorbent (Adsorption Capacity, mg/g)	Ref. Respectively
Cobalt	Olive stone (16); <i>Diplotaxis harra</i> (26); <i>Glebionis coronaria</i> (46); <i>Spirulina sp</i> (96); Activated charcoal (50); Black Tea Waste (15.39)	[126][127][129][147][148]
Zinc	Olive stone (16); Bagasse pith (147); Waste black tea (166.67); <i>Solanum elaeagnifolium</i> (7); Black Tea Waste (12.24)	[55][128][135][148][149]
Iodine	Olive stone (1540); Desert plant (1178); Acorn shell (1209);	[150][151][152]
Phenol	Olive stone (635); Fox nutshell (75); Avocado kernel AC (90); Sawdust	[79][139][153][154]
Chlorophenol	Olive stone (11); Wheat husk biochar (93);	[1][61]
Hg (II)	Desiccated Coconut waste (500)	[155]
As (V)	Sugarcane bagasse (22.1)	[156]
Reactive black 5; Congo red	Coffee waste (77.52; 34.36)	[157]

3.6. Miscellaneous Lignocellulosic-Based Sorbents

Once again, biosorbents are useful for getting rid of pharmaceuticals, pesticides, gas, organic and inorganic contaminants [33]. Mesoporous lignocellulosic-based sorbent from rice straw was fabricated using green protocol [158]. The procedure is environmentally friendly, economically feasible, and can effectively adsorb Pb (II) (952 ± 31 mg/g). This is due to the sulfonic groups, mesoporous nature, and the large surface area [158]. There is much prospect in this for wastewater treatment [158]. Similarly, Peach shell and *Myriophyllum spicatum* were demonstrated biosorbents for Cu, Pb, uranium, and mycotoxins [7]. Furthermore, starbon has been known to preferentially adsorb and separate precious/critical metals at a very low concentration [159]. For this reason, starbon and other bioderived mesoporous materials are considered as suitable for water treatment/purification [18], chromatography [19][91], catalyst supports, drug delivery systems [160], and so on. Methyl blue and Rhodamine decontamination by sugarcane bagasse sorbent has been reported [161]. The methyl blue sorption was independent to the surface area variation unlike Rhodamine. Pehlivan et al. [156] also reported bagasse for the treatment of As (V) (22.1 mg/g). Gusmao et al. modified (using succinic anhydride (SCB 2) and EDTA dianhydride (EB)) sugarcane bagasse for the sorption of ether diamine [162]. The performance capacities of the SCB 2 and EB modified sorbents for ether diamine were 869.6 and 1203.5 mg/g, respectively. At 90 min and pH of 10.0, the equilibrium conditions were attained. Similarly, sawdust has been explored as an abundant and low-cost adsorbent for the removal of dyes [21], phosphate [163], etc. from wastewater with much potential for environmental remediation purposes.

Rice husk adsorbent extracted by sol-gel was used for ampicillin adsorption under batch condition. The optimum temperature and pH for the process are 45 °C and 9, respectively. More so, % removal of ampicillin decreased as adsorbent increased from 0.4–0.6 g [164]. Incinerated rice husk was efficiently applied for treatment of Cu [165]. In addition, rice husk derived AC under carbon dioxide, pyrolysis, and sodium hydroxide is reported [166]. With higher surface area, 899 m²/g, this adsorbent was used for removing methylene blue. Reddy et al. [167] similarly confirmed that H₂O₂-treated rice husk AC adsorbed methylene blue better than AC of peanut shell. Junaid et al. [168] conducted the removal of dyes with rice husk sorbent. The optimal condition was at 240 min contact time, 93% removal, pH 3.0, adsorbent dosage 8.0 g, and dye solution of 200 mL. Gupta and Mote [142] established that saw dust (4.56 mg/g), grain husk ashes (11.11 mg/g), lemon skins (12.65 mg/g), and sugarcane bagasse (5.12 mg/g) performed lower for Cr (VI) sorption than rice husk (16.94 mg/g) [142]. More so, modified banana peels eliminated 95.96%, 100%, 100%, 97.41%, and 76.74% of coloration, TSS (total suspended solids), COD, BOD, and tan plus lignin, respectively [169]. Similarly, Abdulfatai et al. [170] applied peels of banana for sequestration of Zn, Pb, and Cr in wastewater. About 88.9% Cr removal was observed when the peels were activated with 0.5 M sulphuric acids. The decrease in the adsorbent particle size expectedly showed enhanced removal of these heavy metals. Furthermore, the account of Krishni et al. [136] indicated that methyl blue sorption (optimal, 109.89 mg/g) is directly proportional to pH of the solution and the initial concentration using banana leaves sorbent. In another development, 77% removal efficiency of Cr (VI) was achieved using banana peel adsorbent with initial metal concentration 100 mg/L. However, when the amount of metal was decreased, 95% removal was observed [171].

Use of lemon stem sorbent for treatment of aqueous Ni (II) was found to be optimal at pH 5.0, according to Gönen and Serin [172]. The data fitted nicely into Freundlich and Langmuir isotherm models. In addition, Ur (VI) was removed with orange peel from aqueous system [173], with contact time 60 min and pH 4.0 optimal condition. Langmuir model was more suited for the adsorption data. Mafrá et al. [174] treated synthetic aqueous effluent with orange peel adsorbent against Remazol Brilliant blue. Increase in temperature decreased the sorption efficacy. The adsorption data conformed to Freundlich and Langmuir isotherm models. Acid treated coconut coir was applied for the adsorption of cationic and anionic

dye as reported by Ong et al. [175]. The coconut coir showed lower adsorption capacity on anionic dye A07 (10 mg/g) than cationic dye MB (121 mg/g). Ahmad et al. [155] reported optimal sorption capacity of 500 mg/g for Hg (II) with sorbent prepared from waste of coconut milk processing. H₂SO₄ treated coir-pith AC sorbed optimally at contact time 4 h, pH 5.0, Pb concentration of 200 mg/L, and dosage 1 g/L [176]. Coir-pith sorbent activated with ZnC₂ was applied for removal of phenol (92.58 mg/g) by Subha and Namasivayam [177]. Physical and endothermic processes defined the sorption.

Again, adsorption capacity and specific capacitance of tissue paper-derived activated carbon (T-AC) were found to be greater than that of hardboard-derived activated carbon (H-AC) [178]. Further, porous carbon encapsulated transition metal nanocatalysts of commercial tissue paper have been fabricated by ArifulAhsan et al. [179]. Adsorption and desorption behaviors of tetracycline hydrochloride by activated carbon-based adsorbents derived from sugar cane bagasse modified with ZnCl₂ were investigated. This activated carbon showed a high BET surface area of 831 m² g⁻¹ with the average pore diameter and pore volume of 2.52 nm and 0.45 m³ g⁻¹, respectively. The batch experimental results were described by Freundlich equation, pseudo-second-order kinetics, and the intraparticle diffusion model. An amount of 239.6 mg g⁻¹ maximum adsorption capacity was obtained at 318 K. Tetracycline hydrochloride and activated carbon were bonded together by π — π interactions and Cation— π bonds [180].

Moringa oleifera Lam seed adsorbent removed 12.24 mg/g Pb (II) [181]. Meneghel et al. [182] found optimal adsorption of 7.864 mg/g for Cd with *Moringa oleifera* Lam seeds. The optimal conditions were contact time 160 min, pH 7.0, and 400 mg of adsorbent. On the other hand, AC under same condition removed 32.884 mg/g. NaOH-treated *Moringa oleifera* seed removed Mn, 5.61 mg/g (95% removal efficiency) according to Marques et al. [183]. In another development, removal efficiency of 13–100% for organic and inorganic pollutants was found with Olive Stone ACs (OSACs) obtained via chemical activation. On the other hand, the performance of the OSACs obtained by physical activation had removal efficiency ranged between 12% and 99.2% for organic and inorganic pollutants [1]. OSACs have been used for wastewater treatment [1] containing phenol, chlorophenol, nitrophenol, ethanol, iodine, methylene blue dye, remazol red B dye, safranin, amoxicillin, and several heavy metals. Excellently high adsorption capacities of 667, 1495, and 635 mg/g with respect to methylene blue, iodine, and phenol, respectively, had been found. Another extremely high adsorption capacity has been recorded for safranin dye as 526 mg/g [1] using OSAC. More so, high absorption capacities for heavy metals using this ACs was found; lead with 148 mg/g and cadmium with 200 mg/g. It is important to note that the efficiency of the adsorption capacity depends on the method and conditions of activation relative to the adsorbate [1]. Besides these, bioderived sorbents can be used for gas adsorption and storage [184]. Zhao et al. [185] have found significant sorption capabilities for CO₂ (4.3 mmol g⁻¹ at -208 °C and 1 bar) for biocarbonaceous materials. They were selective for CO₂ against N₂ at both low and high temperatures [185]. By extension, biocarbonaceous materials have also been investigated in energy storage. Therefore, broad bean shells S and N dual-doping porous carbon materials were observed to provide specific capacitance of 202 F g⁻¹ and current density of 0.5 A g⁻¹ as cycling performance for electric double layer capacitors [186]. In fact, porous carbon material has the ability of stable performance in lithium ion batteries and sodium ion batteries, and thus can be widely applied in the field of energy storage devices [18][186][187]. Furthermore, recent studies have used biochar as a raw material for electrodes in microbial fuel cells [188] and special supercapacitors [25][189]. In addition, when biocarbonaceous materials are formed at high temperatures (>1200 °C) they become a useful electrode in electrochemical energy and fuel cell [18][36].

4. Shortcomings about Biosorbent Studies

In as much as there are many interests in biosorbents, such studies are dearth of experimental details [1]. Most studies of biosorbents do not have data about pore size distribution, pore volume, functional groups, etc. [22]. In addition, there has been paucity of tailor-made biosorbents for specific pollutant removal. In reality, the pollutant should be defined first, and then one can choose the suitable sorbent, perform preliminary simulation process, optimise, estimate cost, and design the industrial-scale system [1]. It is again important to have a basic/universal standard test for biosorbent. In addition, many of these studies in most cases are lacking feasibility and economic analyses.

References

1. Saleem, J.; Shahid, U.B.; Hijab, M.; Mackey, H.; McKay, G. Production and applications of activated carbons as adsorbents from olive stones. *Biomass Convers. Biorefinery* 2019, 9, 775–802.
2. Aliofkhazraei, M.; Caiado, M.; Farinha, J.; Castanheiro, J.E. Mesoporous Acid Catalysts for Renewable Raw-Material Conversion into Chemicals and Fuel; Comprehensive Guide for Mesoporous Materials. Volume 3: Properties and Development; Nova Science Pub. Inc.: New York, NY, USA, 2015; pp. 67–84.

3. Del Campo, B.G. Production of Activated Carbon from Fast Pyrolysis Biochar and the Detoxification of Pyrolytic Sugars for Ethanol Fermentation. Ph.D. Thesis, Dept. Mechanical Engineering, Iowa State University, Ames, IA, USA, 2015.
4. Demirbas, A.; Ozturk, T.; Demirbas, M.F. Recovery of Energy and Chemicals from Carbonaceous Materials. *Energy Sources Part A Recover Util. Environ. Eff.* 2006, 28, 1473–1482.
5. Nisticò, R.; Lavagna, L.; Versaci, D.; Ivanchenko, P.; Benzi, P. Chitosan and its char as fillers in cement-base composites: A case study. *Bol. Soc. Esp. Cerámica Vidr.* 2019, 59, 186–192.
6. Malhotra, P.; Jaina, A.; Kathal, R. Review on biobased mesoporous material and their application in waste water treatment. *Curr. Trends Biomed. Eng. Biosci.* 2017, 4, 23–25.
7. Stojanovic, M.; Lopičić, Z.; Milojković, J.; Lačnjevac, Č.; Mihajlović, M.; Petrović, M.; Kostic, A. Biomass waste material as potential adsorbent for sequestering pollutants. *Zaštita Mater.* 2012, 53, 231–237.
8. Barakat, M. New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.* 2011, 4, 361–377.
9. Liang, Y.J.; Chai, L.Y.; Min, X.B.; Tang, C.J.; Zhang, H.J.; Ke, Y. Hydrothermal sulfidation and floatation treatment of heavy-metal-containing sludge for recovery and stabilization. *J. Hazard. Mater.* 2012, 217, 307–314.
10. Atkinson, B.; Bux, F.; Kasan, H. Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents. *Water SA* 1998, 24, 129–135.
11. Umar, S.I.; Kutty, S.R.M.; Isa, M.H.; Aminu, N.; Henry, E.; Rahim, A.F.B.A. Biomass as Low-Cost Adsorbents for Removal of Heavy Metals from Aqueous Solution: A Review of Some Selected Biomass; Hassan, R., Yusoff, M., Alisibramulisi, A., Mohd Amin, N., Ismail, Z., Eds.; Springer Science+Business Media: Singapore, 2015; pp. 973–987.
12. Corapcioglu, M.; Huang, C. The adsorption of heavy metals onto hydrous activated carbon. *Water Res.* 1987, 21, 1031–1044.
13. Wang, J.; Chen, C. Biosorbents for heavy metals removal and their future. *Biotechnol. Adv.* 2009, 27, 195–226.
14. Zouboulis, A.; Lazaridis, K.; Karapantsios, T.; Matis, K. Heavy metals removal from industrial wastewaters by biosorption. *Int. J. Environ. Eng. Sci.* 2010, 1, 57–78.
15. Volesky, B. Biosorption and me. *Water Res.* 2007, 41, 4017–4029.
16. Hu, B.; Yu, S.-H.; Wang, K.; Liu, L.; Xu, X.-W. Functional carbonaceous materials from hydrothermal carbonization of biomass: An effective chemical process. *Dalton Trans.* 2008, 5414–5423.
17. Budarin, V.; Clark, J.H.; Luque, R.; White, R. Starbonds®: Cooking up Nanostructured Mesoporous Materials. *Mater. Matters* 2009, 4, 19–22.
18. Varma, R.S. Biomass-Derived Renewable Carbonaceous Materials for Sustainable Chemical and Environmental Applications. *Sustain. Chem. Eng.* 2019, 7, 6458–6470.
19. Lague, R.; Budarin, V.; Shuttleworth, P.S.; Clark, J.H. Anew Star(ch) is Born: Starbonds® as a Biomass-Derived Mesoporous Carbonaceous Materials. Available online: (accessed on 1 April 2021).
20. Reza, M.S.; Yun, C.S.; Afroze, S.; Radenahmad, N.; Bakar, M.S.A.; Saidur, R.; Tweekun, J.; Azad, A. Preparation of activated carbon from biomass and its applications in water and gas purification, a review. *Arab. J. Basic Appl. Sci.* 2020, 27, 208–238.
21. Chikri, R.; Elhadiri, N.; Benchanaa, M.; Maguana, Y.E. Efficiency of sawdust as low-cost adsorbent for dyes removal. *J. Chem.* 2020.
22. Mathew, B.B.; Jaishankar, M.; Biju, V.G.; Beeregowda, N.K. Role of bioadsorbents in reducing toxic metals. *J. Toxicol.* 2016, 2016, 4369604.
23. Fraissard, J.P. *Physical Adsorption: Experiment, Theory, and Applications*; Springer Science & Business Media: Berlin, Germany, 1997; Volume 491.
24. Trapnell, B.M.W.; Hayward, D.O. *Chemisorption*; Butterworths: Oxford, UK, 1964.
25. Hagemann, N.; Spokas, K.; Schmidt, H.P.P.; Kägi, R.; Böhler, M.A.; Bucheli, T.D. Activated carbon, biochar and charcoal: Linkages and synergies across pyrogenic Carbon's ABCs. *Water* 2018, 10, 182.
26. Lehmann, J.; Stephen, J. *Biochar for Environmental Management: Science, Technology and Implementation*; Routledge: Oxford, UK, 2015.
27. Knicker, H. Pyrogenic organic matter in soil: Its origin and occurrence, its chemistry and survival in soil environments. *Quat. Int.* 2011, 243, 251–263.
28. Reisser, M.; Purves, R.S.; Schmidt, M.W.I.; Abiven, S. Pyrogenic carbon in soils: A literature-based inventory and a global estimation of its content in soil organic carbon and stocks. *Front. Earth Sci.* 2016.

29. Sun, T.; Levin, B.D.A.; Guzman, J.J.L.; Enders, A.; Muller, D.A.; Angenent, L.T.; Lehman, J. Rapid electron transfer by the carbon matrix in natural pyrogenic carbon. *Nat. Commun.* 2017, 8, 14873.
30. Román, S.; Libra, J.; Berge, N.; Sabio, E.; Ro, K.; Li, L.; Ledesman, B.; Avarez, A.; Bae, S. Hydrothermal carbonization, Modeling, final properties design and applications, A review. *Energies* 2018, 11, 216.
31. Ani, J.U.; Akpomie, K.G.; Okoro, U.C.; Aneke, L.E.; Onukwuli, O.D.; Ujam, O.T. Potentials of activated carbon produced from biomass materials for sequestration of dyes, heavy metals, and crude oil components from aqueous environment. *Appl. Water Sci.* 2020, 10, 1–11.
32. Weber, B.; Stadlbauer, E.A.; Eichenauer, S.; Koch, C.; Albert, K.; Kramer, M.; Steffens, D. Chemical Nature of Carbonaceous Materials from Biomass by Hydrothermal Carbonization and Low Temperature Conversion. *J. Biobased Mater. Bioenergy* 2013, 7, 367–375.
33. Odetoeye, T.E.; Abu, B.M.S.; Titiloye, J.O. Pyrolysis and characterization of *Jatropha curcas* shell and seed coat. *Niger. J. Technol. Dev.* 2019, 16, 71.
34. Radenahmad, N.; Tasfiah, A.; Saghir, M.; Taweekun, J.; Saifullah, M.; Bakar, A.; Kalam, A. A review on biomass derived syngas for SOFC based combined heat and power application. *Renew. Sustain. Energy Rev.* 2020, 119, 109560.
35. Ukanwa, P.; Sakrabani, A.; Mandavgane, S. A review of chemicals to produce activated carbon from agricultural waste biomass. *Sustainability* 2019, 11, 6204.
36. Chowdhury, Z.Z.; Hamid, S.B.; Das, R.; Hasan, M.R.; Zain, S.M.; Khalid, K.; Uddin, M.N. Preparation of carbonaceous adsorbents from lignocellulosic biomass and their use in removal of contaminants from aqueous solution. *BioResources* 2013, 8, 6523–6555.
37. Chen, Q.; Tan, X.; Liu, Y.; Liu, S.; Li, M.; Gu, Y.; Zhang, P.; Ye, S.; Yang, Z.; Yang, Y. Biomass-Derived Porous Graphitic Carbon Materials for Energy and Environmental Applications. *J. Mater. Chem. A* 2020.
38. Smisek, M.; Cerny, S. Activated carbon. In *Topics in Organic and General Chemistry*; Elsevier Co.: New York, NY, USA, 1970.
39. Stavropoulos, G.G.; Zabaniotou, A.A. Production and characterization of activated carbons from olive-seed waste residue. *Microporous Mesoporous Mater.* 2005, 82, 79–85.
40. Lewis, W.K.; Metzner, A.B. Engineering, design and process development section, Activation of carbons. *Ind Eng. Chem.* 1954, 46, 849–858.
41. Dewar, J. The absorption and thermal evolution of gases occluded in charcoal at low temperatures. *Proc. R. Soc. Lond.* 1904, 74, 122–127.
42. Sheldon, H.H. Charcoal activation. *Phys. Rev.* 1920, 16, 165–172.
43. Weiser, H.B.; Sherrick, J. Adsorption by precipitates. *J. Phys. Chem.* 1919, 23, 205–252.
44. Chaney, N.K. Adsorptive Carbon and Process of Making the Same. U.S. Patent 1497543, 10 June 1924.
45. Metalbank-Co. Zinc Chloride for Activating Charcoal. British Patent 238,889, 1924.
46. Bayer-&Co. Manufacture of Active Charcoal by Briquetting Charcoal Fines and Chemicals under Pressure. British Patents 195,390, 1923.
47. Sutcliffe, E.R. Absorbent and decolorising carbons. *J. Soc. Chem. Ind.* 1924, 43, 635–637.
48. Chaney, N. The activation of carbon. *Trans. Am. Electron. Chem Soc.* 1919, 3, 91.
49. Helbig, W.A. Activated carbon. *J. Chem. Educ.* 1946, 23, 98.
50. Lowry, H.H. On the nature of active carbon. *J. Phys. Chem.* 1929, 34, 63–73.
51. Ruff, O.; Schmidt, G. Amorpher Kohlenstoff und Graphit. *Z. Anorg. Allg. Chem.* 1925, 148, 313–331.
52. Wright, W. Oxidations on charcoal. In *Mathematical Proceedings of the Cambridge Philosophical Society*; Cambridge University Press: Cambridge, UK, 1926; pp. 187–190.
53. Alslaibi, T.M.; Abustan, I.; Ahmad, M.A.; Abu, F.A. Preparation of Activated Carbon From Olive Stone Waste: Optimization Study on the Removal of Cu²⁺, Cd²⁺, Ni²⁺, Pb²⁺, Fe²⁺, and Zn²⁺ from Aqueous Solution Using Response Surface Methodology. *J. Dispers Sci. Technol.* 2014, 35, 913–925.
54. Alslaibi, T.M.; Abustan, I.; Ahmad, M.A.; Foul, A.A. Comparison of activated carbon prepared from olive stones by microwave and conventional heating for iron (II), lead (II), and copper (II) removal from synthetic wastewater. *Environ. Prog. Sustain. Energy* 2014, 33, 1074–1085.
55. Galiatsatou, P.; Metaxas, M.; Kasselouri-Rigopoulou, V. Adsorption of zinc by activated carbons prepared from solvent extracted olive pulp. *J. Hazard. Mater.* 2002, 91, 187–203.

56. Baçaoui, A.; Yaacoubi, A.; Dahbi, A.; Bennouna, C.; Phan, T.L.R.; Maldonado-Hodar, F.J.; Revera Ultrilla, J.; Moreno-Castilla, C. Optimization of conditions for the preparation of activated carbons from olive-waste cakes. *Carbon N. Y.* 2001, 39, 425–432.
57. Albadarin, A.B.; Mangwandi, C. Mechanisms of Alizarin Red S and Methylene blue biosorption onto olive stone by-product, Isotherm study in single and binary systems. *J. Environ. Manag.* 2015, 164, 86–93.
58. Ioannou, Z.; Simitzis, J. Adsorption of methylene blue dye onto activated carbons based on agricultural by-products, Equilibrium and kinetic studies. *Water Sci. Technol.* 2013, 67, 1688–1694.
59. Temdrara, L.; Addoun, A.; Khelifi, A. Development of olivestones-activated carbons by physical, chemical and physicochemical methods for phenol removal: A comparative study. *Desalin. Water Treat.* 2015, 53, 452–461.
60. Rodríguez-Valero, M.A.; Martínez-Escandell, M.; Molina-Sabio, M.; Rodríguez-Reinoso, F. CO₂ activation of olive stone carbonized under pressure. *Carbon* 2001, 39, 320–323.
61. El-Sheikh, A.H.; Alzawahreh, A.M.; Sweileh, J.A. Preparation of an efficient sorbent by washing then pyrolysis of olive wood for simultaneous solid phase extraction of chloro-phenols and nitro-phenols from water. *Talanta* 2011, 85, 1034–1042.
62. Abu-El-Sha'r, W.Y.; Gharaibeh, S.H.; Mahmoud, S. Removal of dyes from aqueous solutions using low-cost sorbents made of solid residues from olive-mill wastes (JEFT) and solid residues from refined Jordanian oil shale. *Environ. Geol.* 2000, 39, 1090–1094.
63. Ubago-Pérez, R.; Carrasco-Marín, F.; Fairén-Jiménez, D.; Moreno-Castilla, C. Granular and monolithic activated carbons from KOH-activation of olive stones. *Microporous Mesoporous Mater.* 2006, 92, 64–70.
64. Tsyntsarski, B.; Petrova, B.; Budinova, T.; Petrov, N.; Teodosiev, D.K.; Sarbu, A.; Sandu, T.; Ferhat, Y.M.; Sirkecioglu, A. Removal of detergents from water by adsorption on activated carbons obtained from various precursors. *Desalin. Water Treat.* 2014, 52, 3445–3452.
65. Menya, E.; Olupot, P.W.W.; Storz, H.; Lubwama, M.; Kiros, Y. Production and performance of activated carbon from rice husks for removal of natural organic matter from water, A review. *Chem. Eng. Res. Des.* 2018, 129, 271–286.
66. Lee, H.W.; Kim, Y.-M.; Kim, S.; Ryu, C.; Park, S.H.; Park, Y.-K.; Info, A. Review of the use of activated biochar for energy and environmental applications Review Articles. *Carbon Lett.* 2018, 26, 1–10.
67. Budinova, T.; Petrov, N.; Razvigorova, M.; Parra, J.; Galiatsatou, P. Removal of arsenic(III) from aqueous solution by activated carbons prepared from solvent extracted olive pulp and olive stones. *Ind. Eng. Chem Res.* 2006, 45, 1896–1901.
68. Yahya, M.A.; Mansor, M.H.; Zolkarnaini, W.A.A.W.; Rusli, N.S.; Aminuddin, A.; Mohamad, K.; Ozair, L.N. A brief review on activated carbon derived from agriculture by-product. *AIP Conf. Proc.* 2018, 1972, 030023.
69. Ao, W.; Fu, J.; Mao, X.; Kang, Q.; Ran, C.; Liu, Y.; Dai, J. Microwave assisted preparation of activated carbon from biomass, A review. *Renew. Sustain. Energy Rev.* 2018, 92, 958–979.
70. Borrero-López, A.M.; Fierro, V.; Jeder, A.; Ouederni, A.; Masson, E.; Celzard, A. High added-value products from the hydrothermal carbonisation of olive stones. *Environ. Sci. Pollut. Res.* 2017, 24, 9859–9869.
71. Aziz, A.; Elandalousi, E.H.; Belhafaoui, B.; Ouali, M.S.; De Ménorval, L.C. Efficiency of succinylated-olive stone biosorbent on the removal of cadmium ions from aqueous solutions. *Colloids Surfaces B Biointerfaces* 2009, 73, 192–198.
72. Silvestre-Albero, A.; Silvestre-Albero, J.; Sepúlveda-Escribano, A.; Rodríguez-Reinoso, F. Ethanol removal using activated carbon, Effect of porous structure and surface chemistry. *Microporous Mesoporous Mater.* 2009, 120, 62–68.
73. Rashidi, N.A.; Yusup, S. A review on recent technological advancement in the activated carbon production from oil palm wastes. *Chem. Eng. J. Biochem. Eng. J.* 2017, 314, 277–290.
74. Hoseinzadeh, H.R.; Wan, D.W.M.A.; Sahu, J.N.; Arami-Niya, A. The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review. *J. Anal. Appl. Pyrolysis.* 2013, 100, 1–11.
75. Stasinakis, A.S.; Elia, I.; Petalas, A.V.; Halvadakis, C.P. Removal of total phenols from olive-mill wastewater using an agricultural by-product, olive pomace. *J. Hazard. Mater.* 2008, 160, 408–413.
76. Gupta, V.K.; Mittal, A.; Malviya, A.; Mittal, J. Adsorption of Carmoisine o from Wastewater Using Waste Materials-Bottom Ash and Deoiled Soya. *J. Colloid Interface Sci.* 2010, 335, 24–33.
77. Kumar, A.; Kumar, S.; Gupta, D.V. Adsorption of phenol and 4-nitro phenol on granular activated carbon in basal salt medium, Equilibrium and kinetics. *J. Hazard. Mater.* 2007, 147, 155–166.
78. Nartey, O.D.; Zhao, B. Biochar Preparation, Characterization, and Adsorptive Capacity and Its Effect on Bioavailability of Contaminants, An Overview. *Adv. Mater. Sci. Eng.* 2014, 2014, 715398.

79. Soudani, N.; Najar-Souissi, S.; Abderkader-Fernandez, V.K.; Ouederni, A. Effects of nitrogen plasma treatment on the surface characteristics of olive stone-based activated carbon. *Environ. Technol.* 2017, 38, 956–966.
80. Tong, Y.; McNamara, P.J.; Mayer, B.K. Adsorption of organic micropollutants onto biochar: A review of relevant kinetics, mechanisms and equilibrium. *Environ. Sci. Water Res. Technol.* 2019, 5, 821–838.
81. Schanz, J.J.; Parry, R.H. The activated carbon industry. *Ind. Eng. Chem.* 1962, 54, 24–28.
82. Smith, A. On the absorption of gases by charcoal. *No I. Proc. R. Soc. Lon.* 1862, 12, 424–426.
83. Marsh, H.; Reinoso, F.R. *Activated Carbon*; Elsevier Science: Amsterdam, The Netherlands, 2006; p. 554.
84. Grand-View-Research-Group. *Activated Carbon Market Analysis by Product (Powdered Activated Carbon (pac), Granular Activated Carbon (gac)), by Application (Liquid Phase, Gas Phase), by End-Use (Water Treatment, Food & Beverages, Pharmaceutical & Medical, A.* Available online: (accessed on 1 April 2021).
85. Hussain, S.; Anjali, K.P.; Hassan, S.T.; Dwivedi, P.B. Waste tea as a novel adsorbent: A review. *Appl. Water Sci.* 2018, 8, 165.
86. Yu, X.; Peng, L.; Gao, X.; He, L.; Chen, K. One-step fabrication of carbonaceous solid acid derived from lignosulfonate for the synthesis of biobased furan derivatives. *RSC Adv. R. Soc. Chem.* 2018, 8, 15762–15772.
87. Zhang, Z.; Yang, S.; Li, H.; Zan, Y.; Li, X.; Zhu, Y.; Dou, M.; Wang, F. Sustainable Carbonaceous Materials Derived from Biomass as Metal-Free Electrocatalysts. *Adv. Mater.* 2018, 31, 1805718.
88. Mezohegyi, G.; van der, Z.F.P.; Font, J.; Fortuny, A.; Fabregat, A. Towards advanced aqueous dye removal processes, A short review on the versatile role of activated carbon. *J. Environ. Manag.* 2012, 102, 148–164.
89. Zhao, F.; Rahunen, N.; Varcoe, J.R.; Chandra, A.; Avignone-Rossa, C.; Thumser, A.E.; Slade, R.C. Activated carbon cloth as anode for sulfate removal in a microbial fuel cell. *Environ. Sci. Technol.* 2008, 42, 4971–4976.
90. Zhang, F.; Cheng, S.; Pant, D.; Van, B.G.; Logan, B.E. Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell. *Electrochem Commun.* 2009, 11, 2177–2179.
91. Shuttleworth, P.S.; Parker, J.; Budarin, V.L.; Breeden, S.W.; Macquarrie, D.J.; Lague, R.L.; White, R.; Clark, J.H. Starbonds®: Preparation, Applications and Transition from Laboratory curiosity to scalable product. *NSTI-Nanotech.* 2011, 3, 766–769.
92. Clark, J.H.; Budarin, V.; Dugmore, T.; Luque, R.; Macquarrie, D.J.; Strelko, V. Catalytic performance of carbonaceous materials in the esterification of succinic acid. *Catal. Commun.* 2008, 9, 1709–1714.
93. Zhu, D.; Pignatello, J.J. Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. *Environ. Sci. Technol.* 2005, 39, 2033–2041.
94. Tan, X.; Liu, Y.; Zeng, G.; Wang, X.; Hu, X.; Gu, Y.; Yang, Z. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere.* 2015, 125, 70–85.
95. Yahya, M.A.; Al-Qodah, Z.; Ngah, C.W.Z. Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production, A review. *Renew. Sustain. Energy Rev.* 2015, 46, 218–235.
96. Thompson, K.A.; Shimabuku, K.K.; Kearns, J.P.; Knappe, D.R.U.; Summers, R.S.; Cook, S.M. Environmental comparison of biochar and activated carbon for tertiary wastewater treatment. *Environ. Sci. Technol.* 2016, 50, 11253–11262.
97. Devi, P.; Saroha, A.K. Utilization of sludge based adsorbents for the removal of various pollutants: A review. *Sci. Total Environ.* 2017, 578, 16–33.
98. Shimabuku, K.K.; Kearns, J.P.; Martinez, J.E.; Mahoney, R.B.; Moreno-Vasquez, L.; Summers, R. Biochar sorbents for sulfamethoxazole removal from surface water, stormwater, and wastewater effluent. *Water Res.* 2016, 96, 236–245.
99. Glaser, B.; Haumaier, L.; Guggenberger, G.; Zech, W. The ‘terra preta’ phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften* 2001, 88, 37–41.
100. Glaser, B.; Balashov, E.; Haumaier, L.; Guggenberger, G.; Zech, W. Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. *Org. Geochem.* 2000, 31, 669–678.
101. Gerlach, H.; Schmidt, H-P. Biochar in poultry farming. *Ithaka J.* 2012, 2012, 262–264.
102. Joseph, S.; Doug, P.; Dawson, K.; Mitchell, D.R.; Rawal, A.; James, H.; Taherymoosavi, S.; Van, Z.L.; Joshua, R.; Donne, S. Feeding biochar to cows, An innovative solution for improving soil fertility and farm productivity. *Pedosphere* 2015, 25, 666–679.
103. Glaser, B.; Lehmann, J.; Zech, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—A review. *Biol. Fertil. Soils* 2002, 35, 219–230.

104. Hilber, I.; Bucheli, T.D. Activated carbon amendment to remediate contaminated sediments and soils: A review. *Glob. N est J.* 2010, 12, 13.
105. O'Toole, A.; Andersson, D.; Gerlach, A.; Glaser, B.; Kammann, C.; Kern, J.; Kuoppamaki, K.; MumMe, J.; Schmidt, H.P.; Schulze, M. Current and future applications for biochar. In *Biochar in European Soils and Agriculture—Science and Practice*; Routledge: Abingdon-on-Thames, UK; Taylor & Francis Group: Abingdon, UK, 2016; pp. 253–280.
106. Schmidt, H.-P.; Wilson, K. 55 uses of biochar. *Ithaka J.* 2012, 29, 286–289.
107. Kuzyakov, Y.; Bogomolova, I.; Glaser, B. Biochar stability in soil: Decomposition during eight years and transformation as assessed by compound-specific ¹⁴C analysis. *Soil Biol. Biochem.* 2014, 70, 229–236.
108. Lehmann, J.; Abiven, S.; Kleber, M.; Pan, G.; Singh, B.P.; Sohi, S.; Zimmerman, A.R.; Stephen, J. Persistence of biochar in soil. In *Biochar for Environmental Management: Science, Technology and Implementation*; Lehmann, J., Joseph, S., Eds.; Routledge: Oxford, UK, 2015.
109. Smith, P. Soil carbon sequestration and biochar as negative emission technologies. *Glob. Chang. Biol.* 2016, 22, 1315–1324.
110. Woolf, D.; Lehmann, J.; Lee, D.R. Optimal bioenergy power generation for climate change mitigation with or without carbon sequestration. *Nat. Commun.* 2016, 7, 13160.
111. Akhtar, A.; Sarmah, A.K. Novel biochar-concrete composites, Manufacturing, characterization and evaluation of the mechanical properties. *Sci. Total Environ.* 2018, 616–617, 408–416.
112. Gupta, S.; Kua, H.W. Factors determining the potential of biochar as a carbon capturing and sequestering construction material, Critical review. *J. Mater. Civ. Eng.* 2017, 29, 04017086.
113. International Biochar Initiative (IBI). International Biochar Initiative—Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil (aka IBI Biochar Standards) Version 2.0; International Biochar Initiative: Westerville, Ohio, 2014.
114. Dorfer, L.; Moser, M.; Bahr, F.; Spindler, K.; Egarter-Vigl, E.; Giullén, S.; Dohr, G.; Kenner, T. A medical report from the stone age? *Lancet* 1999, 354, 1023–1025.
115. Spindler, K. *The Man in the Ice*; Hachette UK: London, UK, 2013.
116. Food and Agriculture Organization of the United Nations (FAO). *Faostat—Forestry Production and Trade*. Available online: (accessed on 6 December 2017).
117. WorldAtlas. st.Laurent, qc Canada. Available online: (accessed on 6 December 2017).
118. United Nations Security Council (UNSC). United Nations Security Council Resolution 2385; UNSC: New York, NY, US A, 2017.
119. Destatis; Federal Statistical Office of Germany: Wiesbaden, Germany, 2016.
120. Kaltschmitt, M.; Hartmann, H.; Hofbauer, H. *Energie Aus Biomasse-Grundlagen, Techniken und Verfahren*; Springer: Heidelberg, Germany; Dordrecht, The Netherlands; London, UK; NewYork, NY, USA, 2009.
121. Brown, R.; del Campo, B.; Boateng, A.A.; Garcia-Perez, M.; Masek, O. Fundamentals of biochar production. In *Biochar for Environmental Management: Science, Technology and Implementation*, Lehmann, J., Joseph, S., Eds.; Routledge: Oxford, UK, 2015.
122. Aziz, A.; Ouali, M.S.; Elandaloussi, E.H.; De Menorval, L.C.; Lindheimer, M. Chemically modified olive stone, A low-cost sorbent for heavy metals and basic dyes removal from aqueous solutions. *J. Hazard. Mater.* 2009, 163, 441–447.
123. Guler, U.A.; Ersan, M.; Tuncel, E.; Dügenci, F. Mono and simultaneous removal of crystal violet and safranin dyes from aqueous solutions by HDTMA-modified *Spirulina* sp. *Process. Saf. Environ. Prot.* 2016, 99, 194–206.
124. Bautista-Toledo, M.I.; Rivera-Utrilla, J.; Ocampo-Pérez, R.; Carrasco-Marín, F.; Sánchez-Polo, M. Cooperative adsorption of bisphenol-A and chromium(III) ions from water on activated carbons prepared from olive-mill waste. *Carbon N. Y.* 2014, 73, 338–350.
125. Lu, J.; Zhang, C.; Wu, J.; Luo, Y. Adsorptive removal of bisphenol A using N-doped biochar made of *Ulva prolifera*. *Water Air Soil Pollut.* 2017, 228, 327.
126. Tounsadi, H.; Khalidi, A.; Abdennouri, M.; Barka, N. Activated carbon from *Diplotaxis Harra* biomass, Optimization of preparation conditions and heavy metal removal. *J. Taiwan Inst. Chem. Eng.* 2016, 59, 348–358.
127. Tounsadi, H.; Khalidi, A.; Machrouhi, A.; Farnane, M.; Elmoubarki, R.; Elhalil, A.; Sadiq, M.; Barka, N. Highly efficient activated carbon from *Glebionis coronaria* L. biomass: Optimization of preparation conditions and heavy metals removal using experimental design approach. *J. Environ. Chem. Eng.* 2016, 4, 4549–4564.

128. Baig, T.H.; Garcia, A.E.; Tiemann, K.J.; Gardea-Torresdey, J.L. Adsorption of heavy metal ions by the biomass of *Solanum Elaeagnifolium* (silverleaf night shade). *Hazard. Waste Res.* 1999, 131, 131–142.
129. Bohli, T.; Ouederni, A. Improvement of oxygen-containing functional groups on olive stones activated carbon by ozone and nitric acid for heavy metals removal from aqueous phase. *Environ. Sci. Pollut. Res.* 2016, 23, 15852–15861.
130. Safari, E.; Rahemi, N.; Kahforoushan, D.; Allahyari, S. Copper adsorptive removal from aqueous solution by orange peel residue carbon nanoparticles synthesized by combustion method using response surface methodology. *J. Environ. Chem. Eng.* 2019, 7, 102847.
131. Van, T.T.; Bui, Q.T.P.; Nguyen, T.D.; Le, N.T.H.; Bach, L.G. A comparative study on the removal efficiency of metal ions (Cu^{2+} , Ni^{2+} , and Pb^{2+}) using sugarcane bagasse-derived ZnCl_2 -activated carbon by the response surface methodology. *Adsorpt Sci. Technol.* 2017, 35, 72–85.
132. Kyzas, G.Z. Commercial Coffee Wastes as Materials for Adsorption of Heavy Metals from Aqueous Solutions. *Materials* 2012, 5, 1826–1840.
133. Bohli, T.; Ouederni, A.; Fiol, N.; Villaescusa, I. Single and binary adsorption of some heavy metal ions from aqueous solutions by activated carbon derived from olive stones. *Desalin. Water Treat.* 2015, 53, 1082–1088.
134. Sreelatha, S.; Jeyachitra, A.; Padma, P. Antiproliferation and induction of apoptosis by *Moringa oleifera* leaf extract on human cancer cells. *Food Chem. Toxicol.* 2011, 49, 1270–1275.
135. Malakahmad, A.; Tan, S.; Yavari, S. Valorization of Wasted Black Tea as a Low-Cost Adsorbent for Nickel and Zinc Removal from Aqueous Solution. *J. Chem.* 2016, 2016, 5680983.
136. Krishni, R.; Foo, K.; Hameed, B. Adsorptive removal of methylene blue using the natural adsorbent-banana leaves. *Desalin. Water Treat.* 2013, 52, 6104–6112.
137. Soudani, N.; Souissi-Najar, S.; Ouederni, A. Influence of nitric acid concentration on characteristics of olive stone based activated carbon. *Chin. J. Chem Eng.* 2013, 21, 1425–1430.
138. Hameed, B.H.; Din, A.T.M.; Ahmad, A.L. Adsorption of methylene blue onto bamboo-based activated carbon, Kinetics and equilibrium studies. *J. Hazard. Mater.* 2007, 141, 819–825.
139. Kumar, A.; Jena, H.M. Removal of methylene blue and phenol onto prepared activated carbon from Fox nutshell by chemical activation in batch and fixed-bed column. *J. Clean Prod.* 2016, 137, 1246–1259.
140. Chatterjee, S.; Kumar, A.; Basu, S.; Dutta, S. Application of Response Surface Methodology for Methylene Blue dye removal from aqueous solution using low cost adsorbent. *Chem. Eng. J.* 2012, 181–182, 289–299.
141. Lyu, H.; Gao, B.; He, F.; Zimmerman, A.R.; Ding, C.; Tang, J.; Crittenden, J.C. Experimental and modeling investigation of ball-milled biochar for the removal of aqueous methylene blue. *Chem. Eng. J.* 2018, 335, 110–119.
142. Gupta, A.; Mote, S. A comparative study and kinetics for the removal of hexavalent chromium from aqueous solution by agricultural, timber and fruit wastes. *Chem. Process. Eng. Res.* 2014, 19, 49–56.
143. Hernáinz, F.; Calero, M.; Blázquez, G.; Martín-Lara, M.A.; Tenorio, G. Comparative study of the biosorption of cadmium (II), chromium (III), and lead(II) by olive stone. *Environ. Prog.* 2008, 27, 469–478.
144. El Nemr, A.; El-Sikaily, A.; Khaled, A.; Abdelwahab, O. Removal of toxic chromium from aqueous solution, wastewater and saline water by marine red alga *Pterocladia capillacea* and its activated carbon. *Arab. J. Chem.* 2015, 8, 105–117.
145. Choudhary, B.; Paul, D. Isotherms, kinetics and thermodynamics of hexavalent chromium removal using biochar. *J. Environ. Chem. Eng.* 2018, 6, 2335–2343.
146. Jeyaseelan, C.; Gupta, A. Green Tea Leaves as a Natural Adsorbent for the Removal of Cr(VI) From Aqueous Solution. *Air Soil Water Res.* 2016, 9, 13–19.
147. Peres, E.C.; Cunha, J.M.; Dortzbacher, G.F.; Pavan, F.A.; Lima, É.; Foletto, E.L.; Dotto, G.L. Treatment of leachates containing cobalt by adsorption on *Spirulina* sp. and activated charcoal. *J. Environ. Chem. Eng.* 2018, 6, 677–685.
148. Mohammed, R.R. Removal of Heavy Metals from Waste Water Using Black Teawaste. *Arab. J. Sci. Eng.* 2012, 37, 1505–1520.
149. Anoop, K.K.; Sreejalekshmi, K.G.; Vimexen, V.; Dev, V.V. Evaluation of adsorption properties of sulphurised activated carbon for the effective and economically viable removal of Zn(II) from aqueous solutions. *Ecotoxicol. Environ. Saf.* 2016, 124, 418–425.
150. Petrov, N.; Budinova, T.; Razvigorova, M.; Parra, J.; Galiatsatou, P. Conversion of olive wastes to volatiles and carbon adsorbents. *Biomass Bioenergy.* 2008, 32, 1303–1310.
151. Bestani, B.; Benderdouche, N.; Benstaali, B.; Belhakem, M.; Addou, A. Methylene blue and iodine adsorption onto an activated desert plant. *Bioresour Technol.* 2008, 99, 8441–8444.

152. Saka, C. BET, TG-DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl₂. *J. Anal. Appl. Pyrolysis*. 2012, 95, 21–24.
153. Rodrigues, L.A.; da Silva, M.L.C.P.; Alvarez-Mendes, M.O.; Coutinho, A.R.; Thim, G.P. Phenol removal from aqueous solution by activated carbon produced from avocado kernel seeds. *Chem. Eng. J.* 2011, 174, 49–57.
154. Larous, S.; Meniai, A.-H. The use of sawdust as by product adsorbent of organic pollutant from wastewater: Adsorption of phenol. *Energy Procedia* 2012, 18, 905–914.
155. Ahmad, M.; Lee, S.S.; Dou, X.; Mohan, D.; Sung, J.K.; Yang, J.E. Effects of pyrolysis temperature on soybean stover and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresour Technol.* 2012, 118, 536–544.
156. Pehlivan, E.; Tran, H.T.; Ouédraogo, W.K.I.; Schmidt, C.; Zachmann, D.; Bahadir, M. Sugarcane bagasse treated with hydrous ferric oxide as a potential adsorbent for the removal of As(V) from aqueous solutions. *Food Chem.* 2013, 138, 133–138.
157. Wong, S.; Ghafar, N.A.; Ngadi, N.; Razmi, F.A.; Inuwa, I.M.; Mat, R.; Amin, N.A.S. Effective removal of anionic textile dyes using adsorbent synthesized from coffee waste. *Sci. Rep.* 2020, 10, 2928.
158. Xu, F.; Zhu, T.T.; Rao, Q.Q.; Shui, S.W.; Li, W.W.; He, H.B.; Yao, R.S. Fabrication of mesoporous lignin-based biosorbent from rice straw and its application for heavy-metal-ion removal. *J. Environ. Sci.* 2016, 53, 132–140.
159. García, A.M.; Hunt, A.J.; Budarin, V.L.; Parker, H.L.; Shuttleworth, P.S.; Ellis, G.J.; Clark, J.H. Starch-derived carbonaceous mesoporous materials (Starbon®) for the selective adsorption and recovery of critical metals. *Green Chem. (RSC)* 2015, 17, S1–S10.
160. Dodson, J.R.; Budarin, V.L.; Hunt, A.J.; Shuttleworth, P.S.; Clark, J.H. Shaped mesoporous materials from fresh macroalgae. *J. Mater. Chem. A*. 2013, 1, 5203–5207.
161. Zhang, Z.; O'Hara, I.M.; Kent, G.A.; Doherty, W.O. Comparative study on adsorption of two cationic dyes by milled sugarcane bagasse. *Ind. Crop. Prod.* 2013, 42, 41–49.
162. Gusmão, K.A.G.; Gurgel, L.V.A.; Melo, T.M.S.; Carvalho, C.; Gil, L.F. Adsorption studies of etherdiamine onto modified sugarcane bagasses in aqueous solution. *J. Environ. Manag.* 2014, 133, 332–342.
163. Benyoucef, S.; Amrani, M. Removal of Phosphate from Aqueous Solution with Modified Sawdust. *Procedia Eng.* 2012, 33, 58–69.
164. Ahile, U.J.; Iorav, H.N.; Dooga, L.; Terungwa, D.; Igbawase, S.D.; Asemave, K. Preparation, Characterization and Application of Rice Husk Adsorbent in the Removal of Ampicillin from Aqueous Solution. *Int. J. Mod. Chem.* 2019, 11, 28–39.
165. Kutty, S.R.; Khaw, S.G.; Lai, C.L.; Isa, M.H. Removal of copper using microwave incinerated rice husk ash (MIRHA) in continuous flow activated sludge system. In *Proceedings of the International Conference on Civil, Offshore and Environmental Engineering (ICCOEE2012)*, Kuala Lumpur, Malaysia, 12–14 June 2012; Universiti Teknologi PETRONAS: Seri Iskandar, Malaysia, 2012.
166. Li, D.W.; Zhu, X.F. Preparation and methylene blue adsorption characteristics of highly mesoporous rice husk active carbon prepared by an Alkali-saving and equipment-friendly method. *Appl. Mech. Mater.* 2014, 448, 182–187.
167. Reddy, P.M.K.; Mahammadunnisa, S.; Ramaraju, B.; Sreedhar, B.; Subrahmanyam, C. Low-cost adsorbents from bio-waste for the removal of dyes from aqueous solution. *Environ. Sci. Pollut. Res.* 2013, 20, 4111–4124.
168. Junaid, M.; Khan, M.U.; Ahmad, F.; Malik, R.N.; Shinwari, Z.K. Rice husk as dyes removal from impregnated cotton wastes generated in sports industries of sialkot. *Pak. J. Bot.* 2014, 46, 293–297.
169. Mohammed, R.R.; Chong, M.F. Treatment and decolorization of biologically treated Palm Oil Mill Effluent (POME) using banana peel as novel biosorbent. *J. Environ. Manag.* 2014, 132, 237–249.
170. Abdulfatai, J.; Saka, A.A.; Afolabi, A.S.; Micheal, O. Micheal. Development of adsorbent from banana peel for wastewater treatment. *Appl. Mech. Mater.* 2013, 248, 310–315.
171. Murthy, U.N. Experimental study on biosorption of Cr (VI) from water by banana peel based biosorbent. *Res. Rev. J. Eng. Technol.* 2013, 2, 37.
172. Gönen, F.; Serin, D.S. Adsorption study on orange peel, removal of Ni (II) ions from aqueous solution. *Afr. J. Biotechnol.* 2014, 11, 1250–1258.
173. Ahmed, M.M. Removal of uranium (VI) from aqueous solution using low cost and eco-friendly adsorbents. *J. Chem Eng. Process. Technol.* 2013, 4, 169.
174. Mafra, M.; Igarashi-Mafra, L.; Zuim, D.; Vasques, É.; Ferreira, M. Adsorption of remazol brilliant blue on an orange peel adsorbent. *Braz. J. Chem Eng.* 2013, 30, 657–665.

175. Ong, S.A.; Ho, L.N.; Wong, Y.S.; Zainuddin, A. Adsorption behavior of cationic and anionic dyes onto acid treated coconut coir. *Sep. Sci Technol.* 2013, 48, 2125–2131.
176. Kumar, P.; Rao, R.; Chand, S.; Kumar, S.; Wasewar, K.; Yoo, C.K. Adsorption of lead from aqueous solution onto coir-pith activated carbon. *Desalin. Water Treat.* 2013, 51, 2529–2535.
177. Subha, R.; Namasivayam, C. Kinetics and isotherm studies for the adsorption of phenol using low cost micro porous ZnCl₂ activated coir pith carbon. *Can. J. Civ. Eng.* 2013, 36, 148–159.
178. Durairaj, A.; Sakthivel, T.; Ramanathan, S.; Obadiah, A.; Vasanthkumar, S. Conversion of Laboratory Paper Waste into Useful Activated Carbon: A Potential Supercapacitor Material and a Good Adsorbent for Organic Pollutant and Heavy Metals; Springer: Berlin/Heidelberg, Germany, 2019.
179. ArifulAhsan, M.; Santiago, A.R.P.; FSanad, M.; Weller, J.M.; OliviaFernandez-Delgado, A.; Barrera, L.; Viridianamuturan, R.; BonifacioAvalrado, T.K.; Chan, C. Tissue paper-derived porous carbon encapsulated transition metal nanoparticles as advanced non-precious catalysts, Carbon-shell influence on the electrocatalytic behaviour. *J. Colloid Interface Sci.* 2021, 581, 905–918.
180. Cai, Y.; Liu, L.; Tian, H.; Yang, Z.; Luo, X. Adsorption and Desorption Performance and Mechanism of Tetracycline Hydrochloride by Activated Carbon-Based Adsorbents Derived from Sugar Cane Bagasse Activated with ZnCl₂. *Molecules* 2019, 24, 4534.
181. Meneghel, A.P.; Gonçalves, A.C.J.; Tarley, C.R.T.; Stangarlin, J.R.; Rubio, F.; Nacke, H. Studies of Pb²⁺ adsorption by *Moringa oleifera* Lam. seeds from an aqueous medium in a batch system. *Water Sci. Technol.* 2014, 69, 163–169.
182. Meneghel, A.P.; Gonçalves, A.C.J.; Rubio, F.; Dragunski, D.C.; Lindino, C.A.; Strey, L. Biosorption of cadmium from water using moringa (*moringa oleifera* lam.) seeds. *Water Air Soil Pollut.* 2013, 224, 1–13.
183. Marques, T.L.; Alves, V.N.; Coelho, L.M.; Coelho, N.M. Assessment of the use of moringa oleifera seeds for removal of manganese ions from aqueous systems. *BioResources* 2013, 8, 2738–2751.
184. Bhadra, B.N.; Vinu, A.; Serre, C.; Jhung, S.H. MOF-derived carbonaceous materials enriched with nitrogen, Preparation and applications in adsorption and catalysis. *Mater. Today* 2018, 25, 88–111.
185. Zhao, L.; Bacsik, Z.; Hedin, N.; Wei, W.; Sun, Y.; Antonietti, M.; Titirici, M.M. Carbon Dioxide Capture on Amine-Rich Carbonaceous Materials Derived from Glucose. *ChemSusChem* 2010, 3, 840–845.
186. Xu, G.; Han, J.; Ding, B.; Nie, P.; Pan, J.; Dou, H.; Li, H.; Zhang, X. Biomass-derived porous carbon materials with sulfur and nitrogen dual-doping for energy storage. *Green Chem.* 2015, 17, 1668–1674.
187. Gao, Z.; Zhang, Y.; Song, N.; Li, X. Biomass-derived renewable carbon materials for electrochemical energy storage. *Mater. Res. Lett.* 2016, 5, 69–88.
188. Huggins, T.; Wang, H.; Kearns, J.; Jenkins, P.; Ren, Z.J. Biochar as a sustainable electrode material for electricity production in microbial fuel cells. *Bioresour Technol.* 2014, 157, 114–119.
189. Jin, H.; Wang, X.; Gu, Z.; Polin, J. Carbon materials from high ash biochar for supercapacitor and improvement of capacitance with HNO₃ surface oxidation. *J. Power Sources* 2013, 236, 285–292.