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The main types of derivatives of plant matter and agricultural waste used as bio-adsorbents for the removal of heavy metals and dyes: a review

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Abstract:

Bio-adsorptions are the most important water treatment products in the world for research in water treatment and the environment, thanks to their effectiveness, simplicity of manufacturing, profitability and low cost compared to other adsorbents. In this context, the present review aims to direct researchers interested in bio-sorption towards derivatives of plant materials and agricultural waste, which present more advantages, such as competitive efficiency, renewal of the raw material, possibility regeneration of the adsorbent several times by a simple treatment, and contribution to sustainability. And in the same context, this review organizes bio-adsorbents derived from plant material into four categories (raw, chemically treated, biochar, activated carbon), depending on the type of treatment of the raw material, and the degree of effectiveness, and presents the most recent examples.

1. Introduction:

Population growth, excessive water consumption, scarcity of water resources, changing wastewater production and various pollution patterns that compromise water sources are causing a real shortae of drinking water in the whole world. For this, wastewater treatment has become a major pain to deal with the problems of lack of fresh water, for daily use and agricultural activities [1]. The dyeing processes of the textile industry alone release between 30,000 and 150,000 t/year of dyes into wastewater [2]. This is a small example capable of giving a clear picture of the annual rate of wastewater in different industries around the world, for which researchers have in recent years opted for wastewater recycling in order to respond to the changing water needs. using several advanced removal processes including chemical precipitation, photocatalysis, flotation, ion exchange, remediation, electrochemical treatment, membrane technologies, adsorption and coagulation/flocculation. These processes are advanced technologies with industrial efficiency and practical relevance. Adsorption and coagulation/flocculation are the most used processes [3].

These techniques have been used for many centuries and are very simple, effective and cost effective and cheaper compared to other techniques used for water treatment by removing suspended particles and dissolved impurities [3]. Generally, the chemicals used in coagulation/flocculation are salts, such as aluminum salts of chemical structure, $(Al_2(SO_4)_3, AlCl_3)$, iron salts $(FeCl_3, FeSO_4)$ [4] and organic polymers as well as acrylamide., acrylic acid and polyacrylamide [5].

Despite their great effectiveness in eliminating suspended and colloidal matter, the coagulation/flocculation treatment technique still

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cannot perfectly eliminate heavy metals and soluble elements. Researchers have recently proven that the remaining traces of these elements cause both very serious threats to living beings and their environment through the intensive diffusion of these chemical reagents during water treatment, which then end up in the waters. . underground or marine ecosystems [6].

Recent research shows that Alzheimer's disease and other acute carcinogenic and genotoxic diseases could be attributed mainly to residual traces of aluminum in treated wastewater [7] [8]. Aluminum salts and metals heavy are harmful agents to health, but they are not the only ones; the majority of commercial polymers are made from petroleum and can pose long-term threats to health. [9]. Today's world and beyond evolving awareness of the effects of these reagents and heavy metals, seeks to avoid these traces in treated water., but we know that it is impossible to completely purify water with these simple techniques, and impossible to use the coagulation/flocculation technique alone to treat water without a second treatment by another more powerful technique, such as the adsorption technique, which allows the elimination of trace elements, and makes adsorption the key technique in the field of wastewater treatment. This technique can be based on plant adsorbents and agricultural waste (not or little recovered), can be improved with low-cost treatments [10].

Adsorption with bio-adsorbents has several other competitive advantages over other wastewater treatment techniques. According to [11] in their comparison of wastewater treatment technologies (photocatalysis, flotation, chemical precipitation, ion exchange, electrochemical treatment, coagulation/flocculation, ultrafiltration, reverse osmosis, nanofiltration and adsorption). Adsorption is classified as a treatment technology with the following characteristics: high metal binding capacity, low cost, high pH variability, ease of use, flexibility and simplicity of design, and low selectivity for heavy metals. The only disadvantage cited is the excessive generation of waste that requires regeneration of the adsorbent for reuse [12] [13]. and other studies that focus on the study of new bio-adsorbents demonstrate that it is possible to regenerate its adsorbents several times. With simple and easy treatments based on hydrochloric acid. Regeneration efficiencies exceed 80% for the first three regeneration cycles. All these characteristics make the use of bio-adsorbents a

simpler, more efficient, economical and sustainable technique.

The objectives of this work are to classify derivatives of plant materials and agricultural waste into 4 categories depending on the type of treatment, the degree of effectiveness and the advantages of each category into four main categories, and discussed on the normative side. , and toxicological and activation processes, and answer questions related to the advantages and disadvantages of these sustainable and economical products, and encourage researchers interested in biosorption to focus on plant-derived bio-adsorbents that possess more advantages, such as renewal, and the possibility of regeneration of the biochar adsorbent for several cycles.

2.   Adsorption:

Adsorption is a very useful, feasible, economical and efficient simple technique used for the removal of pollutants (heavy metals, and dyes) in aqueous solution. the adsorption of the adsorbates in liquid or gas form onto the solid adsorbent is usually achieved by the formation of a chemical or physical bond with the generation of a small amount of sludge and does not require any additional waste management [3], [14]. it is possible to regenerate the adsorbents by desorption from the dung [15].

3.   Adsorbents and bio-adsorbents:

The common used adsorbents are porous chemical carriers or metallic nanoparticles e.g. iron oxide nanoparticles (Fe_2O_3)used to adsorb Chromium (VI), commercial adsorbents with high removal efficiency [16], and (Fe_2O_3/A1SBA-15) are also used to adsorb Chromium (VI) and Arsenic (V) with removal rate of 85 %, and 94 % respectively [17]., Chromium-doped nickel metal nano-oxides are also used to adsorb metal cations such as Cadmium (II), Lead (II) and Copper (II) with a removal rate of (Cd (II), 98%; Pb (II), 99.5%; Cu (II), 97.5%) [18]. Fe_3O_4-$FeMoS_4$ nanoparticles and Magnesium-aluminum double layered hydroxide (MgAl-LDH) are used for the adsorption of metal cations such as Lead (II), Cadmium (II) and Copper (II) with mass yields (Pb (II), 190.75 mg/g; Cd (II) 140.50 mg/g and Cu (II) 110.25 mg/g), [19]. Geo-adsorbents are also often used as reported by [20] using Baluchistan-Pakistan silty clay for the adsorption of Cadmium (II) with a mass yield of 5.48 mg/g, and Nicl with a mass yield of 3.60 mg/g.

The problem of adsorption by metal nanoparticles and geo-adsorbents like clays is the chemical composition itself, most of the nanoparticles contain metal oxide particles like iron and aluminum oxides, among others. Generally, clays that mostly contain aluminosilicates, aluminate ions, tetrahedral silicates, octahedral metal cations, and hydroxyl groups attached to different metal cations, are of lithospheric origin [20].

3.1. Raw bio-adsorbents:

Raw bio-adsorbents are bio-adsorbents without any chemical or thermal modification (physical activation; pyrolysis), they are only the raw material obtained after simple washing, drying, grinding and sieving operations.

The bio-adsorbents [13], [21]-[29] presented in Table 1, are crude derivatives (without any modification) of plant and agricultural materials. The preparation of these bio-adsorbents is easy based mainly on simple operations such as washing, drying, grinding, sieving, and despite the simplicity of the preparation of these bio-adsorbents are capable of eliminating several types of pollutants with remarkable efficiency, for example (Casuarina equisetifolia pines)[21], (The exocarp of chestnuts and almonds)[29] and (Opuntia Ficus Indica Dry)[27], are capable of eliminating Methylene blue with significant levels of 99.41mg/g; 178 mg/g; 90.4% respectively.

This type of derivative is also capable of eliminating heavy metals, for example C(II) ions can be effectively adsorbed with simple bio-adsorbents such as Coffee leaves, tea powder waste and Coffee powder waste which can eliminate C(II) ions. with significant rates 95.15%, 417 mg/g and 526 mg/g [25]-[26], these adsorption rates are very competitive with chemical adsorbents such as [Fe3O4-FeMoS4 nanoparticles and Magnesium-aluminum double layered hydroxide (MgAl-LDH)] which is among the best synthetic adsorbents and can only remove 110.25mg of Cu (II) ions per gram, that is almost 4 times efficiency and more.

Table 1 also presents other examples such as the pods of Parkia speciosa and Lentil ball which can eliminate Pb (II) ions with significant rates 31.36 mg/g, 81.43 mg/g [23], [28]. Brown algae, Sargassumpolycysum which can adsorb up to 105.26 mg/g of Cd (II) [22]. Butternut squash peel waste which can adsorb up to 62.00 mg/g of Cr (VI) [24].

grapfruit peel which can eliminate U (VI) ions with a rate of 140.79 mg/g [13]. The most important thing in these results is that the adsorbents are derivatives of raw plant matter and agricultural waste without any chemical or thermal modification, then are characterized by very important advantages such as the cheapest cost, simplicity of the preparation, biodegradability, sustainable renewal and most importantly that they are not toxic, ecological, and are also an excellent way of valorizing plant waste.

3.2. Activated bio-adsorbents:

Chemically modified bio-adsorbents are bio-adsorbents that have undergone chemical treatments to improve their adsorption capacity by increasing the number of negatively charged binding sites on the bio-adsorbent [30]. According to [31] chemical modifying agents can be acidic (HNO_3 ; H_2SO_4 ; HCL ; $C_4H_6O_6$; $H_2C_4O_2S$) , basic (NaOH ; $Ca(CO)_2$; KOH , or others like Al_2O_3 ; Fe_3O_4 ; $C_8H_4O_3$; CH_2O ; KCl ; $C_{10}H_2O_6$). Table 2 presents chemically modified bio-adsorbents, are derivatives of plant matter or agricultural waste plus a chemical agent generally acid or base, this modification has a remarkable effect on the surface and adsorption capacity for example Agave Bagasse in its raw state the adsorption capacities of Cd (II), Pb (II) and Zn (II) ions are 13.27 mg/g, 35.60 mg/g and 7.84 mg/g respectively and we can note that after the chemical modification with the NaOH base the capacity increases to 18.32 mg/g, 50.12 mg/g and 20.54 mg/g. and after the modification with HCL acid becomes 12.50 mg/g, 42.31 mg/g and 12.40 mg/g, after the modification with nitric acid HNO_3 we obtain other results 13.50 mg/g, 54.29 mg/g and 14.43 mg/g respectively for the same pollutants [38]. Then it can be easily noticed that there is an improvement in the adsorption rate in each case, which shows that the chemical modification plays a very important role in improving the efficiency of the adsorbent.

The table also presents several examples of chemically modified bio-adsorbents which can be competitive alternatives to chemical adsorbents, for example bio-adsorbents which are capable of removing Pb(II) ions such as Neem biomass (leaves & peels) [32], Muskmelon peel (Cantaloupe peel) modified by $Ca(OH)_2$ [34], mercerized garlic peel, native garlic peel modified by NaOH [36] which can adsorb respectively 97.29%, 167.8mg/g, 109.05 mg/g and 51.7 mg/g.

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Table1: Example of some green bio-adsorbents.

Plant	Preparation methods	Pollutant	Adsorption conditions	Removal rate in % or mg/g	Reference
Casuarina equisetifolia pines	- Washing / Drying / Crushing/Sieving	Methylene blue	- 0.5 g adsorbent dose - Optimal pH 7.0	99.41mg/g	[21]
Brown algae, Sargassumpolycysum	- collecting / washing. -Drying under the sun for a day. - controlled drying at 50°C/12hrs. - crushing /sieving at 496.5 nm.	Cd(II)	- the optimal pH 4.65 - Adsorbent dose 1.8 g/L - agitation speed 76 rpm	105,26mg/g	[22]
The pods of Parkia speciosa (PS)	- Collecting /purchasing. - Separation between edible grains and PS seeds. - The seeds were washed several times with demineralized water. -Drying at 60°C in a forced convection oven for 3days. - Cutting into small pieces. -Crushing. -Sieving powder size from 125 to 200 µm.	Pb(II)	- Optimum temperature 55 °C. -concentration initiale de Pb(II) 79,42 mg/L. -pH 4,47 - Adsorbent dose 2 g/L.	31,36 mg/g	[23]
Butternut squash peel waste	- The skin was taken off / Washed - Dried at 60°C - Degreased according to the protocols (AOAC). - Reduced to powder / 40 mesh sieving.	Cr(VI)	- pH 1 - Contact time 40min - Temperature 30°C - Adsorbent concentration 6g/l	62.00mg/g	[24]
Coffee leaves	- Collecting / Washing. - Drying at 70°C. - Grinding with a coffee grinder. - Sieving.	Cu (II)	- Optimal time 48h. -pH 7,5 - Polluted water sample of 250 ml of water from the Mantaro-Orcotuna Rive.	95.15%	[25]
tea powder waste	- Washing several times with bidistilled water - Drying at 70°C/24h. - Crushing / Sieving 500 µm	Cu (II)	- pH = 4 to 4.5 - Cu (II) concentration 1000 ppm. -0.1 g of bio-adsorbent. - Temperature 25°C. - Contact time 40min.	417 mg/g	[26]
Coffee powder waste	- Washing several times with bidistilled water - Drying at 70°C/24h. - Crushing / Sieving 500 µm	Cu (II)	- pH = 4 to 4.5 - Cu (II) concentration 1000ppm. -0.1 g of bio-adsorbent. - Temperature 25°C. - Contact time 40min.	526 mg/g	[26]
Opuntia Ficus Indica Dry	- Crushing / Sieving at ≤40 µm.	Methylene blue	- The dose of DC is 0.6 g/L.	90.4%	[27]
Lentil ball	- Collecting / Washing with tap water - Washing with demineralized water. - Oven drying at 60-70°C until constant weight. - Crushing/ Sieving.	Pb (II)	- Optimal pH, pH= 5.0 - Optimum temperature 30 °C - metal ion concentration of 250 mg/l - Optimal time 60min.	81,43 mg/g	[28]
The exocarp of chestnuts and almonds	- Crushing / Drying at 80 °C for 2 hours. - Extraction and elimination of oils 350g/500ml of hexane for 24h / Filtering. - Washing with hexane and warm water. - Drying/ Crushing /Sieving.	Methylene blue	-50 mg of adsorbent. -20 mL of 300 mg/L methylene blue (MB). - Temperature of 55°C. - Optimal PH equal to 9.	178 mg/g	[29]
grapfruit peel	- Collecting. - Washing with water several times. - Washing with bidistilled water. - Drying at 70°C in a convection oven for 24 hours. - Crushing / Sieving.	U(VI)	- Optimal pH, pH= 5.0 - Optimal contact time (90 min). - The optimal dose of the adsorbent 3.0 g/L	140,79 mg/g	[13]

Table 2: Examples of modified bio-adsorbents.

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Plant	Preparation methods	Pollutant	Adsorption conditions	Removal rate in % or mg/g	Reference
Neem biomass (leaves & peels)	- collecting/Washing with running tap water. - Washing with distilled water. - Drying in the shade for one day. - Drying of the leaves in an oven at 80°C for 7h. - Drying of neem bark at 80°C for 17h/Crushing. - Sieving between (212-500 μm). - Washing several times with distilled water. - Drying for several hours at room temperature. - Storage of the two samples separately. **Activation :** Pre-treatment in one liter of 0.1 N NaOH with agitation at 500 rpm for 1 hour at 25°C. - Sieved to 125 μm and rinsed with distilled water. - Wash several times with deionized water for 45 min at 25°C-/Drying at 55°C for 24 hours. - Drying at 120°C/37 min in 0.73M citric acid at a sample / acid ratio of 1/100 (mass / volume) in a 250 ml flask. The mixture was heated and stirred at 300rpm. / Drying at 50°C/ 24h, then at 120°C/1,5h. - Wash in warm deionized water (60°C) - Drying at 50°C /24 hours.	Pb(II)	- Bioadsorbent dose 0.9 g/L. - Contact time 50 min. - pH 6. - The initial metal ion concentration of 100 mg/L.	97.29%	[32]
Green microalgae (Chlorella vulgaris) modified par H_2SO_4	- After a cultivation of 7 days in specific conditions. - Centrifuged biomass. - Drying in an oven at 80 °C. **Modification :** by 0.1N of H_2SO_4. -Washing with distilled water. - Air drying.	Phenol 2-Chlorophenol	- Contact time = 180 min.	77 % 75 %	[33]
Muskmelon peel (Cantaloupe peel) modified by Ca (OH)$_2$	- Collecting/Washing/Cut into small particles 2mm. **Modification :** -100g mixed with 10g of calcium hydroxide and 500 ml of deionized water for 24h. - Washing up to neutral pH. - Oven drying at 60°C/12h /Crushing -Sieving 300um.	Pb(II)	-pH= 4.5 - Contact time 2h - Temperature 25°C - Adsorbent concentration 5g/l	167.8 mg/g	[34]
Cucumis sativa peels modified by HCl	- Collecting/Washing 1h/Sun drying / 2 days. - Oven drying at 80°C/24h /Crushing. - Sieving 500 μm. - 25 g poured into 250ml of HCl. - Stirred at 250 rpm/4h at 298 K and left overnight. - Wash and filter several times with distilled water until neutral pH / Drying at 85°C for 2 hours.	Cd(II)	-pH 5 - Contact time 1h - Temperature 25°C - Adsorbent concentration 1g/l	58.14 mg/g	[35]
NaOH-modified Egyptian mandarin peel	- Collecting. /1/2 hour wash/Drying at 65°C for 48h. - Crushing. -50 g of PM was soaked in 200 mL ethanol and 100 mL NaOH (0.1N) during 24h. - Filter and wash several times with deionized water until neutral pH. / Oven dried at 65°C/24h. - Crushing./ Sieving (500 mm).	Hg(II)	-pH 6 - Contact time 24h - Temperature 20°C. - Adsorbent concentration 5g/l.	23,26 mg/g	[10]
NaOH-modified mercerized garlic peel	- Collecting. /Washing. /Boiling during 1/2h. -Filtration. / Oven drying at 60°C/24h. - Crushing./ Sieving (100- 300 μm) -10g of product treated with 200mL of 5mol/L NaOH. / Agitation/4h at 25°C./Washing up to pH 7.	Pb (II)	-pH= 7 - Contact time 2h - T= 25°C - Adsorbent concentration 2g/l - Pb^{2+} =100 mg/L.	109,05 mg/g	[36]

Walnut shells with alkaline modification	- Collecting. - Washing. - Crushing. **Modification :** Treatment with 5% NaOH; solid/liquid ratio = 1:5 ; -Drying at 100°C; duration 60 - 180 min. -Washing with distilled water and filtration.	Bleu de Méthylène	-pH =6. - Contact time 240min. -0.2g of bio adsorbent. - Temperature 25°C. - BM concentration =100mg/L.	51.8 mg/g	[37]
Agave Bagasse modified by NaOH (Na-AB)	- Collecting. /Crushing. -Oven drying at 60°C/overnight. / Storage. **Modification:** -25g of RAB soaked in 350mL of 1M NaOH for 6h at 25°C. -Excess NaOH was eliminated by rinsing with demineralized water to neutral pH. - Drying of 60°C/night.	Cd (II) Pb (II) Zn (II)	- Concentration of pollutants 60mg/L. - Optimal pH for adsorption is pH=5 -The optimal temperature 25 °C..	18.32 mg/g 50.12 mg/g 20.54 mg/g	[38]
NaOH-modified native garlic peel	- Collecting. / Washing. / Boiling during 1/2h. -Filtration. - Oven drying at 60°C/24h. - Crushing. - Sieving (100- 300 μm) -10g of product treated with 200mL of 5mol/L NaOH. - Agitation/4h at 25°C. - Washing up to pH 7.	Pb (II)	-pH 7 - Contact time 2h - Temperature 25°C - Adsorbent concentration 2g/l	51,7 mg/g	[36]
(1)-Dragon fruit peel (2)-Rambutan peel (3)-Passion fruit peel (Modified by H_2SO_4)	- Collecting. / Washed with tap water 3 times. - The peels have been cut into small pieces. - Crushing./Drying under the sun for one week. - Drying in an oven at 60°C for 24 hours. - Reduction to fine powder. - Washed separately with distilled water three times. - Sieving of 10 to 20 mesh. **Modification** - Treatment with H_2SO_4 (4 mol/L) during 30 min. - Wash several times with distilled water. - Drying in the oven at 60°C for 24 hours.	Cu (II)	- Dose of bio-adsorbent 0,25 g. - Contact time 180 min. - Initial concentration of 100 mg/L. -Optimal pH = 4 -Optimal pH = 5 for (3) - Ambient temperature.	92,593 mg/g 192,308 mg/g 121.951 mg/g	[39]

And other heavy metals such as Cd (II) ions with an effectiveness of 58.14 mg/g by Cucumis sativa peels modified by HCl [35], and Hg (II) ions by Egyptian mandarin peel modified by NaOH with an efficiency of 23.26 mg/g[10], and Cu(II) ions by bio-adsorbents such as Dragon fruit peel 92.593 mg/g, Rambutan peel 192.308 mg/g and Passion fruit peel (Modified by H_2SO_4) with a capacity of 121,951 mg/g [39].

This category of bio-adsorbents is also capable of eliminating organic pollutants and dyes, for example Walnut shells with alkaline modification which can adsorb Methylene Blue with a rate of 51.8 mg/g [37]. And Green microalgae (Chlorella vulgaris) modified by H_2SO_4 which is capable of adsorbing Phenol and 2-

Chlorophenol with rates of 77% and 75% respectively [33].bio-adsorbents in this category are effective and can be economical (depending on the cost of the chemical material used for modification), the production of this type of bio-adsorbent is simpler than chemical adsorbents, and can be a best way to recycle plant waste.

4. Biochar and activated carbon:
4.1. Biochar:

Biochar or bio-carbon is a black, porous, low-density, amorphous, and stable carbonaceous material derived from the carbonization of various plant materials. Biochars have multifunctional properties [15], frequently used as bio-adsorbents for the removal of organic and inorganic pollutant molecules due to

their porous properties, rich in active sorption sites, [40]–[44]. They are typically pyrolytic byproducts of biological-vegetal feedstocks that have a high density of biodegradable organic matter and are therefore unsuitable as adsorbents [41], [43], [45]–[48].

The high temperature of pyrolysis moderated by a controlled calcination speed, degrades organic structures into small gaseous carbon dioxide, water, and other molecules in an inert or weakly oxidizing environment. This process leaves behind porous carbon structures with surfaces rich in functional groups, which characterize the physicochemical properties of biochar. Moreover, the oxygen-containing functional groups are found in biochar produced by pyrolysis under completely inert 100% nitrogen atmospheres than those produced under air [49].

The physicochemical properties of biochars are mainly related to two factors: the pyrolysis temperature and the sources of raw materials, including surface substitution, functional groups, hydrophobicity [50]–[54]. The surfaces of the active adsorption sites are rich in single and double carbon-carbon covalent bonds, OH-, and aldehyde CHO-functions, COOH-carboxylic functions, aromatic carbon skeletons, metal-O/OH-oxides, inorganic crystal phases, and other functional groups. The great difference in the properties of the biochar surface functional groups is the origin of the multifunctional adsorption of biochar [7], [36], [44], [47], [55]–[58].

To evaluate the influence of pyrolysis temperature on biochar properties, a wide range of feedstocks are studied. The main results of this study are that increasing the pyrolysis temperature increases the biochar pH, surface area, pore size, ash content, hydrophobicity, and elemental ratio (O/C) to elemental ratio (H/C) (ratios indicating stability) and negatively impacts other properties such as, biochar yield, [15]. On several types of raw materials, results that were almost identical were detected in the pyrolysis temperature range of 200-800 °C. Carbon concentration, aromaticity, pH, ash content, surface area, stability and pore size all rise as pyrolysis temperature increase, whereas biochar yield, hydrogen content, oxygen content, elemental ratios (H/C) and (O/C) decrease [54], [59], [60].

The same pyrolysis temperature applied to a wide range of feedstocks does not produce biochar with the same physico-chemical properties [36], [61], [62]. Due to the variances in chemical composition and contents of cellulose, hemicellulose, lignin and inorganic minerals, the raw materials response to specific pyrolysis conditions are often different from one another [15], [63]–[65]. Hence, the efficiency and the physical-chemical properties of the biochar depend on the used material chemical composition and pyrolysis conditions which are still a lack of clear and consistent transparent information.[15], [66].

Biochar is an adsorbent with multifunctional physico-chemical characteristics, capable of adsorbing various types of pollutants thanks to various types of functional groups on the pore surfaces of biochars. The type and nature of the raw material and the pyrolysis conditions favor some types of functional groups over others and consequently increase the adsorption of some types of pollutants over others due to the affinity of the pollutant with the functional group, which negatively impacts the multifunctionality and improves the selectivity of one type of pollutant by the biochar [15].

4.2. Raw materials used for the production of biochars and examples of applications:

From foregoing, it can be concluded that the source materials for biochar and activated carbon are all organic substances of plant origin with high carbon content and low ash content, e.g. peat [67] , rice straw [68], beer dregs [69], palm kernel husks [70], native sugarcane bagasse waste [71] pistachio nuts and shells [72], coffee, tea, mint and cistus [26], [73], wood [74], [75], molasses [76].Table 3 describes some examples of raw biochars.

Biochar is also a very effective form of derivatives of plant materials and agricultural waste, based on the pyrolysis of raw bio-materials without any chemical modification, the conditions of the pyrolysis such as the temperature and duration of the pyrolysis play a role very important in the efficiency and elimination rate of biochar for example Camellia seed husk biochar at (700°C).

Better than Camellia seed husk biochar at (300°C) in removing Pb (II) and Cd (II) ions, at 700°C can remove 89.03% and 75.84%, and at 300°C only 80.61%, 53.57% respectively [82]. And this proves that increasing the pyrolysis temperature can play a very important role in improving the elimination of pollutants, table 3 presents several other effective examples on heavy metals of these biochars such as Coconut shell biochar [80] and Peanut shell [84] which can remove Cd (II) ions with rates of 80% and 99.9% respectively, and Banana peel biochar [79] which can remove Cu ions (II) with a rate of 351 mg/g

equivalent to a percentage of 96%. Orange peeling and Bagasse from sugar cane biochars which can respectively remove 27.86 mg/g and 86.96 mg/g of Pb (II) ions [81].biochars are also capable of eliminating organic molecules and dyes, for example Cactus biochar [83] capable of eliminating Methylene blue with a rate of 102 mg/g, and Chinese palm biochar [77] and biochar from Mint extraction Waste [78] which

can remove rates of 21.4 mg/g and 322.58 mg/g of Malachite green respectively.

Biochars are truly real competitors of chemical adsorbents in terms of cost and effectiveness, and have several advantages such as simplicity of preparation, effective regeneration for several cycles, is not toxic for the environment, and it is effective solution for the recovery of plant waste

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Table 3: Examples of raw biochar.

Plant	Preparation methods	Pollutant	Adsorption conditions	Removal rate in % or mg/g	Reference
Chinese palm	- Collecting. / Manual separation. - Wash several times with deionized water. - Sun drying for 5 days. - Drying in an oven set at 100°C. - Pyrolysis at 500°C for 4h with speed of 5°C/min. The biochar produced - Washing with hot sterile deionized water. - Dehydrated at 100°C for 24 hours.	Malachite green	-pH =2. - Adsorbent dose = 1 g/L. - Contact time =24h. - Temperature =35°C.	21.4 mg/g	[77]
Mint extraction Waste	- Collection of mint waste after oil extraction. - Oven drying at 60-80 C for 4h. - The resulting stems, after removing the leaves, were crushed (30-50 mm) - Pyrolysis of 400°C/2h. - Sieving (<0.21 mm).	Malachite green	- Agitation = 180 rpm. - Temperature =32°C - Contact time = 10min. - The optimal pH is between 6 and 8.	322.58 mg/g	[78]
Banana peel	- Drying in the sun for 11 days (29°C) - Oven drying 65°C/2h. - Crushing -pyrolysis at 500°C or 600°C for 3 h in a tube furnace with nitrogen gas circulating at 20 ml/min.	Cu(II)	- Cu(II) solution (1000 mg/l) was prepared by dissolving $Cu(NO_3)_2$ and $Pb(NO_3)_2$ in distilled water.	351 mg/g equivalent to a percentage of 96%	[79]
-Coconut shell -a local soil of Sri Lanka (Entisol) -(1:1 mixture of biochar and soil)	- Drying - Crushing - Pyrolysis - Mixing with soil.	Cd(II)	- The range of pH $\geq$ 3, the initial pH of the solution had a minor effect on removal efficiency.	80%	[80]
-Orange peeling -Bagasse from sugar cane	- Collecting. - Washing. - Drying 7 days in the air. - Oven drying at 80°C/2 days. - Carbonization.	Pb (II)	- Preparation of a series of standard Pb (II) ion concentrations of 6, 30, 57, 112 and 223 mg/L. - The pH of the prepared solutions was adjusted to values ranging from 2 to 6	27.86 mg/g 86,96 mg/g	[81]
Camellia seed husk (700°C)	- Collecting. - Washing 3 times with distilled water. - Dried at 80°C for 48 hours. - Pyrolyzed in a tube furnace under nitrogen at 700°C.	Pb (II) Cd (II)	- optimal pH = 5.0 ± 0.1. - The initial concentration =150mg/L -Temperature = 298.15K	89,03 % 75,84 %	[82]
Camellia seed husk (300°C)	- Collecting. - Washing 3 times with distilled water. - Dried at 80°C for 48 hours. - Pyrolyzed in a tube furnace under nitrogen at 300°C.	Pb (II) Cd (II)	- The optimal pH = 5.0 ± 0.1. - The initial concentration =150 mg/L.	80.61 % 53,57 %	[82]

			- Temperature = 298.15 K.		
Cactus	- Collecting. - Washing. - Drying in an oven at 80 °C. - Crushing. - Calcination for 4 h at 300 ° C.	Methylene blue	-100 mg of carbonized solid powder. -pH = 8 - Temperature 25 °C - The dye concentration is 200 mg/l	102 mg/g	[83]
Peanut shell	--------	Cd (II)	- Contact time 12 hours. - pH of 5.0, - Initial Cd concentration of 200 mg/l - Adsorbent dose 40g/l, - Temperature 25°C	99,9%	[84]

4.3. The polarity of biochar:

The abundance of polar or non-polar functional groups is controlled mainly by the pyrolysis of organic feedstock rich in cellulose, hemicellulose, and lignin producing a wide range of polar oxygen-containing functional groups, but low mass yields of biochar. In contrast, a higher proportion of lignin leads to a higher yield of biochar with non-polar functional groups, and this is simply due to the thermal stability of the aromatic monomers compared to the aliphatic structures of cellulose and hemicellulose.

The increase in pyrolysis temperature also favors non-polar functional groups due to the loss ofthermally sensitive hydroxylic and aliphatic groups [85]–[90].

Therefore, biochars produced at low temperatures are in most cases hydrophilic due to the presence of a wide range of polar oxygen-containing functional groups [66]. In contrast, biochars derived at higher temperatures are more likely to contain aromatic structures and backbones, resulting in hydrophobic functional groups [66], [87], [91], [92]. The hydrophilic or hydrophobic properties of biochar can be enhanced by different techniques, such as steam activation, the impregnation method, chemical and thermal treatments [93].

4.4. Mechanism of biochar formation:

The mechanism of transformation of organic raw material into biochar is a complicated one. It starts with dehydration, depolymerization and goes through several processes of radical decomposition and radical restructuring, under the effect of high pyrolysis temperature, hemicellulose and cellulose are more thermo-sensitive than lignin is fragmented and transformed faster than lignin. Cellulose is mainly se-decomposed by depolymerization into

oligosaccharides and redevelops glycosidic bonds to produce d-glucopyranose and levoglucosan. Levoglucosan dehydrates to levoglucosenone, which then undergoes several processes including decarboxylation, dehydration, aromatization and condensation to form biochars,[7], [88], [94], [95].

On the pyrolysis temperature scale, at less than 200°C to 300°C, the raw materials start to decompose exactly from 300°C to 350°C, cellulose and hemicellulose start to degrade, which is characterized by the formation of a wide range of ketonic, alcoholic, and phenolic functional groups, among others. From 300°C to 600°C, a wide range of aliphatic functional groups derived from cellulose and hemicellulose begin to degrade [66], [96] and from 600°C to 900°C, benzene derivatives and polycyclic structures begin to form through transformations [66], [95], but for lignin, the mechanism is purely radical, starting with the breaking of β -O-4 bonds, which generate free radicals that can initiate a radical chain reaction to the most thermodynamically stable molecular form and the formation of biochar [88], [96], [97]. A description of the detailed mechanisms of lignin, cellulose, and hemicellulose decomposition during pyrolysis, has been described in the work of Liu et al. [96], despite the lack of a complete understanding of the detailed processes of lignin pyrolysis, which remain unknown [15]. By effect of pyrolysis temperature, the metals in the feedstock remain in the biochar in the form of refractory oxides, such as Fe_2O_3 , SiO_2 , KCl, Al_2O_3 , $CaSO_4$, and $CaCO_3$[98].

4.5. Activation of carbon:

In the minds of researchers, the word "coal" is automatically linked with the word activated coal, where active is the description of the operation of coal activation, and activation is a general description of the particular preparation of coal for the purpose of

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developing the degree of porosity and characteristics of the coal surface.

According to Kwiatkowski et al.,2019 [99], [100], there are two methods of carbon activation: physical activation and chemical activation, with the possibility of combining both.

1)   Physical activation is typically performed after carbonization in an inert atmosphere at 500-800 °C, followed by controlled gasification either steam or carbon dioxide in the typical temperature range of 700-1,100 °C. Carbon dioxide activation results in better development of micropores (< 2 nm) and especially ultra-micropores (< 0.7 nm), whereas steam results in a more uniform structure. Carbon dioxide activation results in a better development of micropores (< 2 nm) and especially ultra-micropores (< 0.7 nm) at 1100 °C, while steam results in a structure with a wider distribution of micropores and a higher fraction of meso-pores [101], [102].

2)   Chemical activation consists of the use of a chemical agent for activation; in this case, the activation is simultaneous with the pyrolysis of the raw material impregnated with the activating agent; after the pyrolysis, the excess activating agent and by-products must be leached out in order to reveal the porous structure, the higher impregnation usually leads to high porosity and a high contact surface. The activating agent, pyrolysis temperature, activation atmosphere, and impregnation rate are the factors thataffect the formation of the pore structure during chemical activation [100]–[103].

Chemical activation agents are both drying and oxidizing, and reduce the production of volatiles, which increases the efficiency of chemical activation. The shorter the activation time than the physical activation, the lower temperature. Generally, chemically activated carbons have a larger specific surface area and pore volume than those produced by physical activation [102], [104], [105], whereas chemical activation is more efficient, simpler, and cheaper on the energy side [100].

4.6. The chemical activation:

Chemical activating agents are often inorganic acids such as sulfuric, phosphoric and nitric acids.
But organic acids, bases and salts, etc., can also be used. The type of activating agent plays a very important role in this operation, and can modify the

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characteristics of a coal depending on the activation solution.

For a raw material such as hazelnut shells, activated carbons with potassium hydroxide (KOH) have both high surface areas and a moderate degree of surface heterogeneity, while activated carbons with phosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$) characterized by the highest microporous surface and the highest surface heterogeneity [102].

It can be said that activated carbons are the most complicated derivatives in the manufacturing procedure compared to the other 3 categories of derivatives of plant materials and agricultural waste, possessing competitive effectiveness with chemical adsorbents. And table 4 presents several examples of these activated carbons, for example Activated biochar from Bael fruit shell activated by H_3PO_4, capable of eliminating Cu (II) and Pb (II) ions with rates of 92% and 79% respectively [115], the charcoal of the Egyptian mandarin peel Activated by H_2SO_4 acid capable of adsorbing Hg (II) ions with a rate of 34.84 mg/g[10], the charcoal of Citrulluslanatus activated by NaOH capable of adsorbing U (VI) ions with a rate of 27.61 mg/g[106], Activated biochar derived from Sesbaniabispinosa capable of eliminating As (V) ions with a rate of 12.47 mg/g [110]. Other examples such as charcoal from Auricularia auricula activated by CS_2 [108] and Activated biochar derived from Rice straw [109] both are capable of eliminating Cd(II) ions with rates of 458.35 mg /g and 126.52 mg/g respectively. This category of derivatives is also capable of eliminating organic pollutants in an effective manner such as Activated biochar derived from Anthriscus sylvestris capable of eliminating organic pollutants, Diclofenac (DF) and Cephalexin (CPX) with significant rates of 392.94 mg/g and 724.54mg/g [113]. And the carbon from Orange fruit peel waste Activated by H_3PO_4 is capable of eliminating Methylene Blue with an adsorption rate of 96.02% [116]. Activated biochar derived from pig manure and Activated biochar derived from Rice straw both are capable of eliminating Tetracycline with significant rates 552.0 mg/g and 365.7 mg/g respectively [107].

There are several advantages of using activated carbons from plant materials and agricultural waste in water treatment, the first is that they are economical compared to synthetic adsorbents but are the most expensive compared to other types of derivatives, can simply prepare compared to synthetic chemical adsorbents, have high regeneration rates for several cycles, and generally have more porosity and contact surface compared to other categories of bio-adsorbents, and can be a better way to valorize plant and agricultural waste

Table 4. Examples of biochar chemically activated

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Plant	Preparation methods	Pollutant	Adsorption conditions	Removal rate in % or mg/g	Reference
Citrulluslanatus activated by NaOH	- Washing with ultrapure water. - Air drying. - Crushing - Pyrolysis at 350°C for 15 min. - Cooling. / Drying. - Adding a 0.3 M iron (II) sulfate heptahydrate solution. - Add 100 mL of potassium permanganate solution. / Agitation. - Add NaOH solution (up to pH 10). - Agitation for 3 hours. / Centrifugation - Rinse with ultrapure water. - Drying at 50°C for 24 hours.	U (VI)	- Quantity of biochar of 0.05 g. -50 ml of uranium. - Filtration with a 0.2 syringe filter. - Optimum temperature is 318K.	27.61mg/g	[106]
(1)Activated biochar derived from pig manure (2)Activated biochar derived from Rice straw	- Collecting. - Washing. - Heated to 700°C/2h. - Crushing. - H_3PO_4 activation with drying at 105°C/24h.	Tetracycline	- Stirring speed is 200 rpm at 25°C. - Centrifugation at 3000 rpm for 20 min. -Filtration (0,45 μm). - Initial concentration of Tetracycline (30-200 mg/L). - The optimal pH is 9. - Contact time is 168 h	552,0mg/g 365,7 mg/g	[107]
Auricularia auricula activated by CS_2	- Drying /Washing/Crushing. - Sieving (0.25 mm). - Pyrolysis at 400°C for 120 min. - Preparation of a solution of 240 ml NaOH (0.4 M) and 360 ml CS2. - Agitation at 25°C for 5h. - Ultrasound treatment for 1/2 h - Mixing of the solution prepared with biochar (ratio of 1/10). - Shaking at 40°C for 5 hours. - Filtering. /Drying..	Cd (II)	- Adsorbent dose is 2 g/L. - Pollutant volume of 100 ml. - The optimal pH is 5. - Ionic strength of 0.01 mol/L. - Optimum temperature is 298K	458.35 mg/g	[108]
Activated biochar derived from Rice straw	- Collecting /Washing with distilled water. - Drying at 60°C for 24 h. / Crushing. - Mixed with a solution of sodium phytate. - Ratio (mass of 1:5). - Agitation for 12 hours. - Drying at 60°C for 48 hours. - Pyrolysis at different temperatures for 2h.	Cd (II)	- Biochar dose of 25 mg. - Cd(II) of 25 mL. - Temperature =25°C. - Agitation = 220 rpm. - Filtration through a 0.45 μm membrane. - pH=6	126.52 mg/g	[109]
Activated biochar derived from Sesbaniabispinosa	- Cutting in small pieces. - Rinsing with DI water. / Air drying. - Pyrolysis 450 °C for 1 hour. - Crushing (< 0.25 mm). - Rinsing. /Drying. / Storage. - Preparation of CuO nanoparticles. - Mixing of the two solutions (0.25 g of SBC). / Stirring for 10 min. - Addition of 50 ml of KOH (0.15M). - Filtration. / Drying at 90°C for 40 min. - Calcination at 350°C for 50 min.	As (V)	- Ambient temperature (25 ± 1.5 °C). - The optimal pH is 4. - The adsorbent dose is 1.0 g/L. 10 mg of As/L	12.47mg/g	[110]
Activated biochar derived from cotton shell	- Drying at 70°C for 24 hours. - Pulverization. - Pyrolysis at 350°C for 2 hours. - Crushing. - Activation with H_3PO_4 (2.5/1) for 6h	Sulfadiazine	- SDZ concentration is 10 mg/L. - The biochar dose is 1.0 g/L - Agitation speed is 120 rpm. - Filtration with a membrane of 0.45 μm. - Contact time is 12 h. - Optimal temperature is 298k	86.89mg/g	[111]
Activated biochar derived from Grapefruit zest	- Cutting in pieces. - Drying at 105°C to a constant weight.	Pb (II)	- The optimal pH was between 5.3 and 6.5.	12.73mg/g	[112]

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	- Crushing. / Sieving. - Activation by (ZnCl$_2$) 15% with the ratio (1:3)/12h - Pyrolysis at 600°C/1h./Soaked in 1%HCl. - Washing up to neutral pH. - Dried at 85°C/12h		- Contact time 1.5h		
Activated biochar derived from Anthriscus sylvestris	- Drying at 45 ° C for 1 day. - Grinding. - Sieving at 250 µm. - Combustion at 300°C for 15 minutes. - Modification with 4 M NaOH. - Drying at 105°C overnight. - Heating to 600°C for 2 hours. - Washing with water and HCL. - Drying at 45°C overnight.	Diclofenac (DF) Cephalexin (CPX)	- Stirring speed of 80 rpm for 24 h. - The DF dose is 50 mg/L. - The CPX dose is 30 mg/L. - The dose of biochar is 0.1 g/L. - Optimum temperature is 298K. - The optimal pH for DF is 6. - The optimal pH for CPX is 4.	392.94 mg/g 724.54 mg/g	[113]
Activated biochar derived from Neem peel	- Collecting. - Washing. - Drying. - Crushing. - Chemical activation. - Pyrolysis.	Zn (II) Cu (II)	- Contact time is 48h. - Adsorbent dose 6 g/L. - The temperature is 35°C. - The optimal pH is 1.2	11.90mg/g 21.23 mg/g	[114]
Bael fruit shell activated by H$_3$PO$_4$	- Collecting. /Washing. /Drying. /Crushing. - Sieving in the size range of 500 to 860 µm. - Activation with a ratio (1:1) H$_3$PO$_4$ (85%) - Drying at 100°C for 4 to 5 h. - Pyrolysis at 600°C. - Then 2% sodium bicarbonate. - Drying at 100°C for 4 h.	Cu (II) Pb (II)	- The adsorbent dose of 2 g. - Optimal Cu (II) concentration of 100 ppm. - Optimal pH : pH = 7	92 % 79 %	[115]
Orange fruit peel waste Activated by H$_3$PO$_4$	- Drying. - Crushing. - Sieving. - Drying and carbonization at 200 °C for 2 hours. - Chemical activation with H$_3$PO$_4$	Methylene Blue	- A constant MB concentration of 100 ppm. - A temperature of 60°C	96.02 %	[116]
Egyptian mandarin peel Activated by H$_2$SO$_4$ acid	- Collecting. /Washing. /Cutting. /Drying. -100g added to 80mL of 98% H$_2$SO$_4$ for 2h. - Boiling/2h in an efficient hood Cooling in an ice bath. - The mixture poured on 0,5L of cold water. -Filtration. - Heated in an oven at 180˚C for 2h.	Hg (II)	-pH= 6 - Contact time 24h. - Temperature 20°C. - Adsorbent concentration 5g/l.	34,84mg/g	[10]

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- Immersed in 0.5 L of 5% NaHCO$_3$. - Wash with distilled water to pH 6. - Drying in an oven at 150˚C for 12h. cooling -crushing -sieving				

4.7. Toxicity and quality standards for biochar:

4.7.1. Toxicity of biochar:

Despite the advantages of activated carbons in wastewater treatment, some researchers have just assessed the impact of harmful biochar components such as dioxins, heavy metals, polycyclic aromatic hydrocarbons, free radicals, volatile organic compounds and perfluorinated chemicals [117]–[122].

[123] revealed in their work that the above-mentioned toxic elements have adverse effects on the environment, and may be present in biochar.

The source of heavy metals in biochar is the biochar feedstock, and of course biochar is made from sewage sludge, which has the highest heavy metal content, whereas the concentration of heavy metals in biochar is generally related to the feedstock.

Concerning the polycyclic aromatic hydrocarbons present in biochar, their content depends on the biochar production process, which increases when the pyrolysis temperature and/or the residence time in the kiln decrease. The contents of free radicals increase with increasing pyrolysis temperatures [124].

Similarly, the formation of dioxins is related to the biochar production process, specifically the decrease of pyrolysis temperature [117]The presence of chlorine derivatives is mainly related to the chloride content of the raw material [125]. Similarly, volatile organic compounds and perfluorinated chemicals may be formed during the pyrolysis process of organic polymers such as lignin, cellulose, and hemicellulose [126], and most plant materials rich in lignin and cellulose, 80% of the coconut shell is the endocarp of the palm tree are capable of being easily transformed by pyrolysis into (82.23%) of volatile materials [127].

4.7.2. The standards of biochar:

Certain harmful components in biochar, such as polycyclic aromatic hydrocarbons, benzo(a)pyrene, polychlorinated biphenyls, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and heavy metals, are subject to several standards.

Technical standards and voluntary certificates such as the International Biochar Initiative-Biochar Standard (IBI-BS) for the USA [128], the Biochar Quality Mandate (BQM) for the UK [129], and the European Biochar Certificate (EBC) for the European Union [130]. There are also other standards published by the International Organization for Standardization (ISO), such as (ISO 5946:2022 Bamboo-based activated carbon - General specifications), the first edition of which was recently published in October 2022 by the Technical Committee: ISO/TC 296 Bamboo and Rattan, ICS: 75.160.40 Biofuels [131]). This standard contributes directly to the sixth goal on clean water and sanitation [132], and the twelfth goal on responsible consumption and production, for the establishment of sustainable consumption and production patterns [133]. The rapid growth and development of bamboo-based activated carbon makes it necessary to establish an international standard to guide production, quality requirements, and international trade. There are also almost 79 technical standards relating to the production and quality control of coals, methods of determination and assay of trace elements, the chemical composition of coals, and related recommendations drafted by the teams of ISO Technical Committee 27. The majority of these standards concern combustible coals [134].

In Morocco there is a Draft Moroccan Standard PNM EN 12915-2 / IC 03.2.282/2023 relating to Chemical Products used for the treatment of water intended for human consumption - Part 2: Reactivated granular activated carbon, and it is the only standard that deals with adsorbents in Morocco[135], and concerning the legal side there is an absence of laws relating to the use of bio-adsorbents, in the Moroccan legislative regulations relating to water treatment.

Due to the little amount of activated carbon produced globally, the guidelines that do exist govern biochar production rather than end-use applications [123].

5. Regeneration of bio-adsorbents:

Bio-adsorbents and especially pyrolyzed forms (biochar and activated carbons) have a high regeneration capacity e.g. bio-adsorbents based on grapefruit peel can be regenerated several cycles, the results for the first three cycles exceeded 80% recovery using hydrochloric acid (0.05 mol/l) [13]. In addition, experimental results show that after four cycles of regeneration, the adsorption capacity increased from 94.6% to 85.2% using hydrochloric acid 0.1N [12].

6. Comparison between bio-adsorbents and chemical adsorbents:

Wastewater treatment researchers can easily say that generally activated carbons are the best adsorbents than any other chemical adsorbents especially in terms of cost, porosity, efficiency and contact surface, but there are some natural bio-adsorbents in the raw state without any modification or activation either thermal or chemical which can be better even than activated carbons, then we can say with confidence that there are always bio-adsorbents (either activated or raw) equivalent to chemical adsorbents in terms of performance and more economical in terms of cost, for example the synthetic adsorbent (Chromium-doped nickel metal nano-oxides), capable of adsorbing Cd (II) with a rate of 98% [18], there is a natural bio-adsorbent (Peanut shell) which can adsorb at a rate of 99.9% [84], then (peanut shell) is a more effective and more economical alternative, of natural origin capable to be renewed naturally, the same for the pollutants Pb (II) and Cu (II), the same synthetic adsorbent capable of eliminating Pb (II) with a rate of 99.5% and Cu (II) with a rate of 97.5%, there is the Neem biomass bio-adsorbent (leaves & peels) which can remove up to 97.29% of Pb (II) [32], so it can be an excellent alternative for adsorbents chemicals. And for copper, coffee leaves [25] and Coffee powder waste [26], can eliminate respectively 95.15% and 526 mg/g of Cu (II) ions and this without any type of treatment, by this efficiency this bio -adsorbent can replace any other type of chemical and synthetic adsorbents, the table also presents other examples of bio-adsorbents which can easily replace chemical adsorbents. with the same logic, natural bio-adsorbents also capable of eliminating organic dyes with very high efficiency, and the best-known examples in this context are Casuarina equisetifolia pines for the adsorption of Methylene Blue with a rate of 99.41 mg /g [21], and

Mint extraction Waste for adsorption of Malachite green with a rate of 322.58 mg/g [78].

Table 5: Comparison of pollutant removal rates for some examples of bio-adsorbents and chemical adsorbents.

Adsorbents	Pollutants	Elimination rate	reference
Chromium-doped nickel metal nano-oxides	Cd (II) Pb (II) Cu (II)	98% 99.5% 97.5%	[18]
Fe$_3$O$_4$-FeMoS$_4$ nanoparticles and Magnesium-aluminum double layered hydroxide (MgAl-LDH)	Pb (II) Cd (II) Cu (II)	190.75mg/g 140.50mg/g 110.25mg/g	[19]
Fe$_2$O$_3$/A1SBA-15	Cr (VI) As (V)	85 % 94 %	[17]
Coffee powder waste	Cu (II)	526 mg/g	[26]
Coffee leaves	Cu (II)	95.15%	[25]
Neem biomass (leaves & peels)	Pb (II)	97.29%	[32]
Butternut squash peel waste	Cr (VI)	62.00 mg/g	[24]
Activated biochar derived from Sesbaniabispinosa	As (V)	12.47mg/g	[110]
Peanut shell	Cd (II)	99,9%	[84]
Camellia seed husk (700°C)	Pb (II) Cd (II)	89,03 % 75,84 %	[82]
Casuarina equisetifolia pines	Methylene Blue	99.41mg/g	[21]
Mint extraction Waste	Malachite green	322.58mg/g	[78]

7. discussion and perspectives:

According to the work of the researchers cited in this work we can say that the 4 categories of bio-adsorbents are real competitive alternatives to chemical and synthetic adsorbents in terms of cost, simplicity of manufacturing process, durability, and most importantly c is efficiency. And in terms of efficiency specifically we can classify the 4 derivatives, from the least effective to the most effective for the same raw material, we base ourselves on the work of the researchers cited, we can say that theoretically the efficiency increases in function of the degree of activation of the raw material from (++) for the raw material without any modification up to (+++++) for the activated carbon form of the same raw material. And table 6 gives the advantages and the degree of effectiveness of each category of derivatives of plant matter and agricultural waste.

Despite the absence of a complete study on the increase in efficiency according to all the possibilities of activation in a successive manner for the same raw material, but according to the existing studies carried

out on activation, and the remarkable improvement in the adsorption rates after activation, we can say that it is only necessary to seek the optimal conditions of activation for each plant raw material or agricultural waste, to obtain a more effective derivative, and it It is necessary to carry out a series of successive activation operations to obtain the best possible derivative.

Unfortunately, rarely where studies are carried out on several pollutants more than 3, most cases it is only 1 pollutant per study, and it is certain that bio-adsorbents can eliminate several pollutants especially the biochar and activated carbon forms. thanks to the non-selective nature of charcoal, the example of the natural bio-adsorbent (Peanut shell) in charcoal form which can adsorb a rate of 99.9% of Cd(II) [84], but the work is only carried out on Cd(II) ions, and it is certain that this adsorbent can adsorb other pollutants with similar percentages or less thanks to the porosity and the non-selective nature of the carbons. There are also other very effective examples in this work and are not studied on other pollutants such as the bio-adsorbent of Neem biomass (leaves & peels) activated by the NaOH base, which can eliminate up to 97.29% of the Pb (II) [32], but coffee derivatives remain the most economical and profitable bio-adsorbents in terms of effectiveness/cost ratio, such as coffee leaves and Coffee powder waste [25], [26], which can eliminate respectively 95.15% and 526 mg/g of Cu (II) ions without any type of physical or chemical treatment

then these bio-adsorbents are more effective and more economical alternatives, of natural origin capable of being renewed naturally in a sustainable manner, and regenerated for several cycles, especially the biochar and activated carbon forms which can be regenerated by treatments acid [12],[13], and after the exhaustion of these bio-adsorbents they can be reused as coal fuels or additives in the cement industry.

Table 6: the degree of effectiveness and advantages of the 4 categories of bio-adsorbents.

The type of derivative of plant matter	The advantages	Efficiency
Raw without any modifications	-The most economical; -the simplest preparation; -The most ecological; -Renewable; -Biodegradable; -is not toxic; -recovery of plant waste.	**Can be effective**++ (Depending on the surface characteristics and porosity of the raw material)
Chemically modified	-can be economical (depending on the cost of the chemical material used for the modification); -simpler manufacturing than chemical adsorbents; -recovery of plant waste.	**More efficient +++** Improvement of functional contact surface groupings
Physically Modified (biochar)	-economic; -simple preparation; -Regenerable for several cycles; -is not toxic; -recovery of plant waste; -more porosity and contact surface.	**More efficient ++++** Improved contact surface
Physically and chemically modified (activated carbon)	-economical compared to synthetic adsorbents but the most expensive compared to other types of derivatives; -simple preparation; -Regenerable for severalcycles; -valorisation des déchets végétales. -plus de porosité et de surface de contact.	**More efficient +++++** Surface enhancement and functional surface groupings

7. Conclusion:

The use of plant-based bioadsorbents for wastewater treatment can provide a dual solution to existing problems: firstly, it offers an environmentally friendly, competitive, cost-effective and reliable approach to water treatment, and second, it transforms underutilized plant materials into valuable wastewater treatment materials. Bioadsorption is the most cost-effective method of water treatment, and plant-derived bioadsorbents are the most cost-effective adsorbents available. These bio-adsorbents can be used in various forms, including raw, chemically treated, biochar and activated carbon, these 4 categories of derivatives are cost-effective and competitive, and several examples prove that these bio-adsorbents are the treatment products of the future, such as the bio-adsorbent of Neem biomass (leaves & peels) activated by the NaOH base, which can adsorb 97.29% of Pb (II) [32], and the biochar of (Peanut shell) which can remove up to 99.9 % of Cd(II) [84], and this adsorbent rate is incomparable with industrial adsorbents, but despite the high elimination rate, coffee derivatives remain the most economical, most available bio-adsorbents, the most ecological and the most profitable in terms of efficiency/cost ratio, such as coffee leaves and Coffee powder waste [25], [26], which can eliminate respectively 95.15% and 526 mg/g of Cu (II) ions. and this in the raw state of the raw material, without any type of treatment.

Bio-adsorbents derived from plant matter and agricultural waste, offering a competitive advantage over industrial adsorbents. However, the potential risk of generation of toxic elements during the pyrolysis process, as well as the scarcity of normative studies, pose challenges to technology transfer from laboratory to industrial scale. Despite extensive research on bioadsorbents, several challenges and issues need to be addressed before their widespread implementation. Further research is needed to assess the economic and technical aspects on a large scale. Although the adsorption efficiency and mechanism of bioadsorbent have been well studied, attention should also be paid to the desorption of pollutants. Additionally, exploring the regeneration of bioadsorbents is another important area to explore further. Most studies on biochar have been conducted in the laboratory and with only one pollutant present. Therefore, future research should include the study of bioadsorbents in the presence of coexisting analytes or multiple pollutants separately.

8. Declaration of competing interests:

The authors declare that they have no known competing financial interests or personal relationships that might appear to influence the work reported in this article.

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10. References:

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