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Application of Agricultural Waste from Main Brazilian Crops as Adsorbent for Wastewater Treatment

Aplicação de Resíduos Agrícolas das Principais Culturas Brasileiras Usados como Adsorventes para o Tratamento de Efluentes

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Adsorption is a powerful method for wastewater treatment. The adsorbent materials used are limited due to the high cost of production and for their difficult regenerability. This work aims to show the importance of reusing agricultural residues, transforming them into efficient adsorbent materials. Highlighting the growing interest in the subject through bibliometric analysis and punctuating the main preparation techniques with direction for specific characteristics desired in the materials, understood through the main techniques of physical and chemical characterization. It will also be shown the economic and quantitative relevance for Brazil of some agricultural crops of worldwide occurrence, as well as the potential of transforming their residues into adsorbent materials for the treatment of effluents. Finally, studies involving real effluents will be presented, corroborating the efficiency of these materials and the possibility of future industrial applications. This set of information presents the reader with a valuable amount of information about the real possibility of reusing agricultural solid waste as a powerful tool in the treatment of urban and industrial effluents, thus increasing reuse and attacking two important environmental problems.

Keywords: Bibliometric analysis; agricultural waste; low-cost adsorbents; wastewater treatment.

1. Introduction

Population growth, and the inherent need to meet the demands of a vast number of people, promotes the emergence of issues which endanger the delicate balance in ecological systems around the world. Among these problems, a spotlight must be placed upon the cumulative effect of man-made products, which, in large scale, is potentially devastating to environmental resources.[1] The finitude of natural and hydric resources, as well as the production solid, liquid and gas residues, manufactured through conventional production methods propel the search for efficient and sustainable technologies, and the development of research that improve processes and minimize environmental impacts.[2]

The rise in biomass uses as food, forage, bioplastic, biofuel, and bioenergy tends to significantly impact agricultural production, since the application of these products emerges as an alternative to natural resources demand. Such use has increased the portion agriculture occupies in the world economic scenario.[3] Agricultural development is one of the most powerful tools against extreme poverty and hunger and might be the only way to feed an ever-growing population, which, according to estimates, will reach 9.7 billion people by 2050.[4]

Biomass comes from a wide variety of living organisms: animals, plants, microorganisms etc. Concerning agricultural biomass, an ample diversity of products derives from plant raw material processing and, consequently, the quantity of liquid, solid and gas residues produced is proportionally colossal. Among them, lignocellulosic solid waste, with high organic matter content and deriving out of human and animal food, is responsible for large environmental impacts: disposal of biomass, which takes place during harvest and processing, creates billions of tons of garbage annually. The requirement of a more productive and sustainable agriculture drives the search for new systems of production and processing, reusing or recycling raw material residues, linked to a circular economy concept and based upon reducing the waste disposal through a new chain of added value products.[5]

Brazil is one the world titans in the agribusiness and, in the last 40 years, has shown expressive increase in productivity. Nevertheless, such escalation depends on several parameters: population numbers; average income and consumption; technology innovation; land appreciation; preservation of natural resources; agricultural policies; environmental laws; regulation marks;

and international agreements.[6] According to the Brazilian Institute of Geography and Statistics (IBGE), Brazil is a leading player in the production of a number of crops: cotton, peanut, rice, oat, banana, cocoa, coffee, sugarcane, cashew, maze, soil, sorghum and wheat. In 2022, a steep increase in tonnage harvested was observed in several of the abovementioned crops, from which the more pronounced were seen in coffee, cotton, sorghum, peanut, beans, wheat and maize, with yield raises of 9.7%; 15.0%; 21.0%; 27.0%; 27.0%; 27.3% and 37.4% respectively.[4,7]

Accompanying the expressive food harvests, there is a proportional boost in the quantity of residues generated, and inadequately disposed. A rising tendency employed to mitigate this problem is the application of biomass as fertilizers, fuel material and adsorbents. According to the Food and Agriculture Organization of the United Nations (FAO), the world agroindustry production of residues reached 1.3 billion ton a year in the last decade, and one third of this was attached to wastage in the food industry.[8]

The usage of agriculture residues as adsorbents in wastewater treatment is becoming frequent due to the growing concern with the scarcity of hydric resources. This process takes advantage of the biomass capability of efficiently, and safely, removing pollutants via adsorption in fluids. They are not, however, the only adsorbents available; other materials, such as active carbon, zeolites and clays are also employed to the same end.[9] Notwithstanding, plant biomass is a promising source for adsorbents due to the low cost, it is widely available and easy to obtain, in addition to possessing inherent interesting adsorptive properties, namely: high surface area, rugosity, morphology, and pore sizes.

Due to Brazilian monumental territorial extension, there is a massive diversity in biomass sources for researchers to study, among which it is imperative to highlight sawdust, husks, fruit seeds and bagasse, almond seed, sugarcane, grains, legume plants and mate.[10] Agriculture residues in Brazil come from different sectors, due to the country's diversified economic matrix and ample extension. Therefore, in consonance with the production of goods and products, there is also the generation of residues. Using these otherwise discarded materials is an auspicious alternative to reduce natural resources extraction and pollutant accumulation. And, as a perk, this option increments the sustainability and economic value of the industry.[11]

There are several methods employed in the treatment of liquid effluents. The most efficient techniques are: adsorption, membrane filtration, reverse osmosis, precipitation, electrochemical treatments, and ionic exchange.[12] Standing out of these processes, adsorption has become a method of choice to treat large volumes of effluent, due to the efficiency, sustainability, low cost, and feasibility it provides.[13]

Adsorption is a well-known, efficient and economic method used to remove impurities in liquid effluents. It is based on a mass transfer phenomenon where molecules present in the fluid layer (adsorbate) adhere to a solid surface (adsorbent).[14] Adsorption can occur through physisorption, chemisorption, ionic exchange or microprecipitation, due to electrostatic or chemical interactions which take place on the surface of the material, i.e., it is a surface adhesion phenomenon.[15]

Using natural adsorbents in wastewater treatment has shown interesting results in the removal of a wide range of water-soluble contaminants, even the ones known as persistent pollutants, which get this label due to their unusual resistance and recalcitrance to conventional techniques. Some examples that are part of this class are: micropollutants[16]; textile dyes[17]; oil spill[18]; pharmaceuticals[19]; heavy metals[20]; and biocides[21].

Bearing the information mentioned above in mind, the present work aims to demonstrate the potential applications of biomass derived from important Brazilian crops as sources of natural adsorbent materials used in the environment remediation and circular economy, through the transformation of agricultural residues into added value products. These absorbents, that otherwise would be seen as waste, are employed in efficient and sustainable treatment of liquid effluents.

2. Agricultural Residues used as Adsorbents in Effluent Treatment: Bibliometric Analysis

A bibliometric analysis was carried out in October 2022, based on the search in the Scopus database of the terms adsorbent ("ADSORBENT"), agricultural residues ("AGRICULTURAL WASTE") and effluent treatment ("WASTEWATER TREATMENT") in the title, abstract and keywords from articles and reviews published in scientific journals written in English. Figure 1 presents the number of publications over time. The search returned 330 scientific articles, divided into 253 articles with original research data and 77 critical review articles, with a significant increase in production in the last six years.

The author who published the most on the topic was Vinod Kumar Gupta (six articles), from the University of Johannesburg, South Africa, followed by Alok Mittai (five articles), from the National Institute of Technology, India. The ten authors with the highest number of publications are shown in Figure 2a. The countries with the highest number of publications are India, China and Malaysia (Figure 2b) and the journals with the most articles are *Desalination and Water Treatment*, *Chemosphere* and *Bioresource Technology* (Figure 2c). Notably, this is a multidisciplinary topic that arouses interest in lines of research related to the areas of environment, energy, chemistry and engineering. The dominant areas of study, illustrated in Figure 2d, are environmental sciences (226), chemical engineering (92), chemistry (84), and engineering (64). However, it is noteworthy that the Scopus categories do not limit the

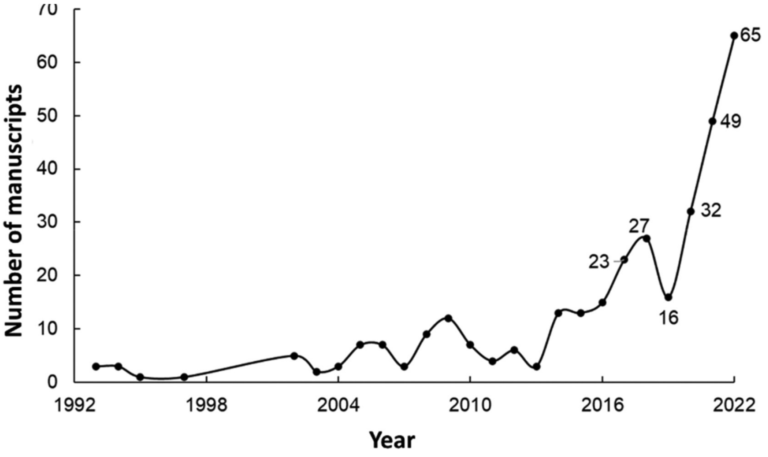

Figure 1. Publications containing the terms adsorbent, agricultural residues, and effluent treatment in the title, abstract and keywords: number of articles published per year.

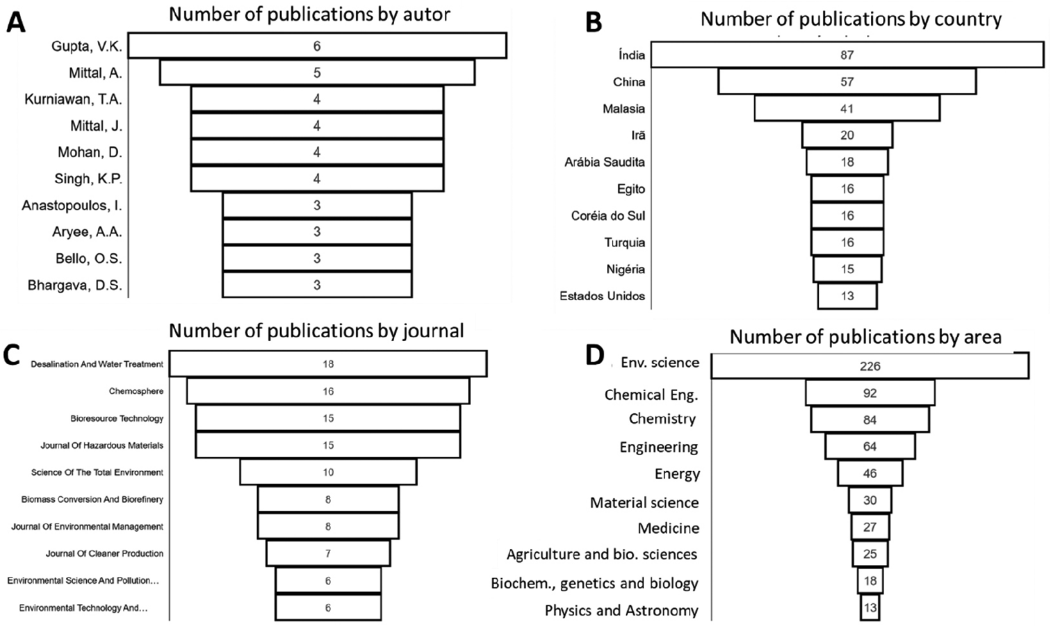

Figure 2. Bibliometric analysis of publications containing the terms adsorbent, agricultural residues and effluent treatment in the title, abstract and keywords: number of articles published by author (a), by country (b), by journal (c) and by study area (d).

articles to just one area, meaning that a publication can be related to several areas of knowledge.

Keyword analysis has gained special attention recently, as it can help to understand the evolution of studies in a given area and analyze the trend of the themes explored. Publications on the topic began in the 1990s, with eight articles published. The first three articles were published in 1993, in the same issue of the journal *Water Research*.[22,23,24] The works investigated the potential for phosphate removal by activated carbon from tamarind nutshell, a low-cost and abundantly available material. The following year, three studies were published using other residues, namely activated charcoal from peanut shells to remove cadmium in effluents[25], coconut fiber to treat dyeing effluents[26] and pine bark pretreated with acidified formaldehyde solution to remove heavy metals Zn^{2+}, Cu^{2+} and Pb^{2+}.[27] Other articles published in the 1990s were critical reviews on the use of soybean and cottonseed husk by-products, rice straw and sugarcane bagasse as adsorbents for metal ions in aqueous solutions[28] and different adsorbent materials used in the treatment of industrial pollutants, including low-cost residues.[29] In this decade, only seven keywords appeared in five articles or more, as shown in Figure 3.

In the 2000s, 55 articles were published, with 74 keywords presented in Figure 4. In this decade, in addition to critical reviews and experimental research, a wide range of agro-industrial residues began to be explored, with attractive determinants of low cost and High Availability. The most cited articles in this decade investigated the use of chitosan, biomass, bagasse, coconut husks, peanuts, almonds, wheat, soybeans, almonds, apricot seeds, cherry and ash, among other agricultural residues.[30-35]

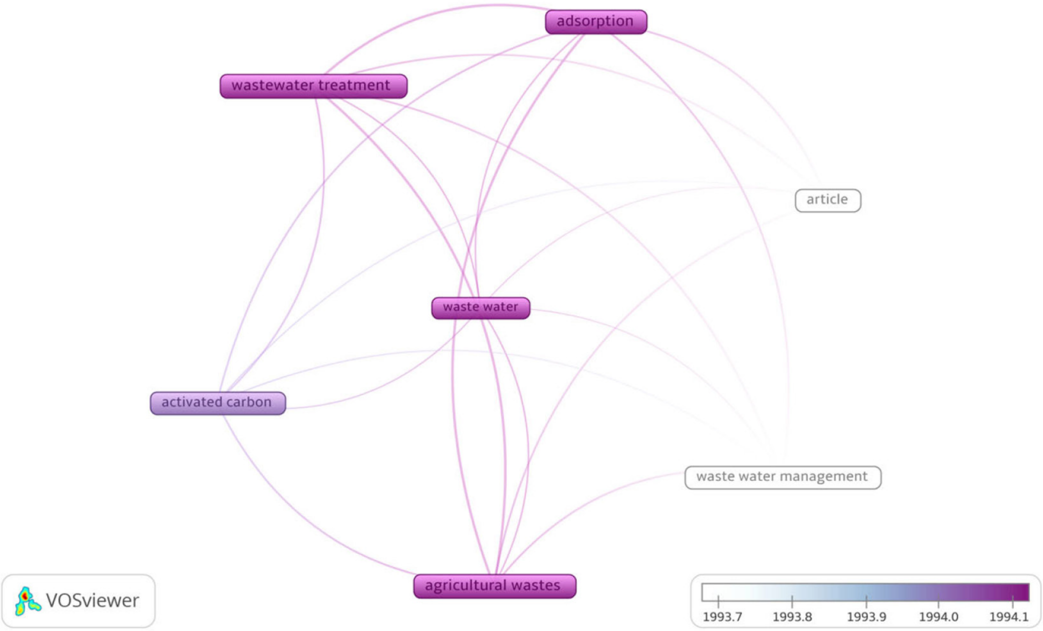

Figure 3. Keywords used by the authors in articles on adsorbents made from agricultural waste for use in effluent treatment in the period between 1991 and 2000.

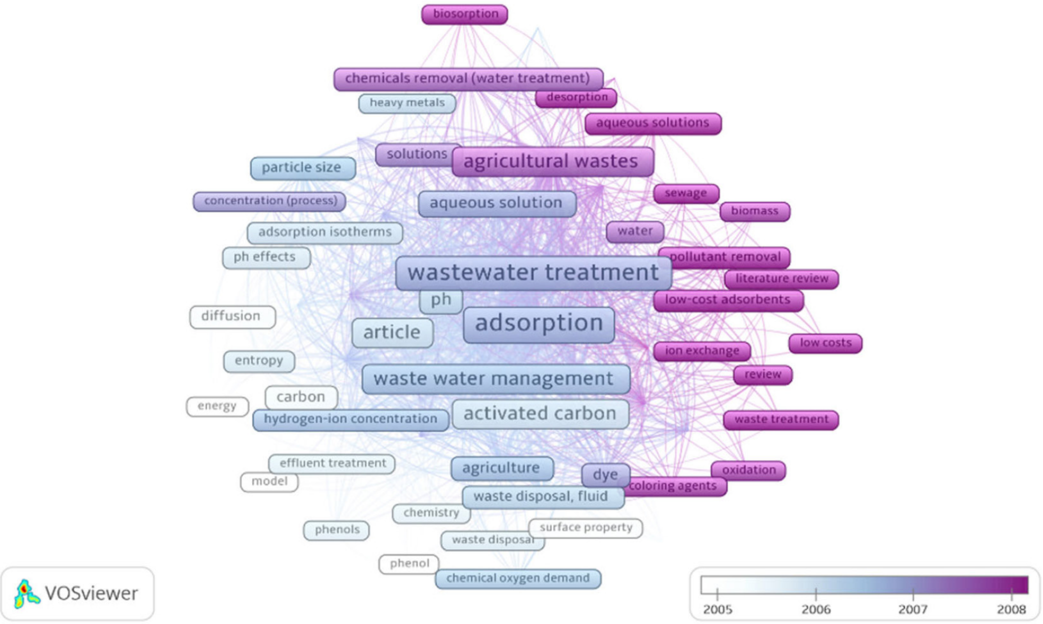

Figure 4. Keywords used by the authors in articles on adsorbents made from agricultural waste for use in effluent treatment in the period between 2001 and 2010.

In the 2010s, 152 articles were published, with 156 keywords shown in Figure 5. In this decade, review and experimental articles were published comparing different agricultural residues. The terms present in the most cited articles included agricultural waste husks, green adsorbent, low-cost materials, biochar technology in wastewater treatment, magnetic biochar from agricultural waste biomass and agricultural solid waste adsorbents.[36-42]

In the years 2021 and 2022, 115 articles were published, with 112 keywords shown in Figure 6. In these two years, the topics become more advanced and diversified, such as critical reviews of activated carbons and composites prepared from of biomass from agricultural residues, comparative studies using experimental and advanced modeling, application of modification methods associated with adsorption studies, applications in CO capture and sorption of pollutants in wastewater and exhaust gases in adsorbents incorporated from residual resources and nanomaterials.[43-47]

Table 1 presents the most cited articles by other authors

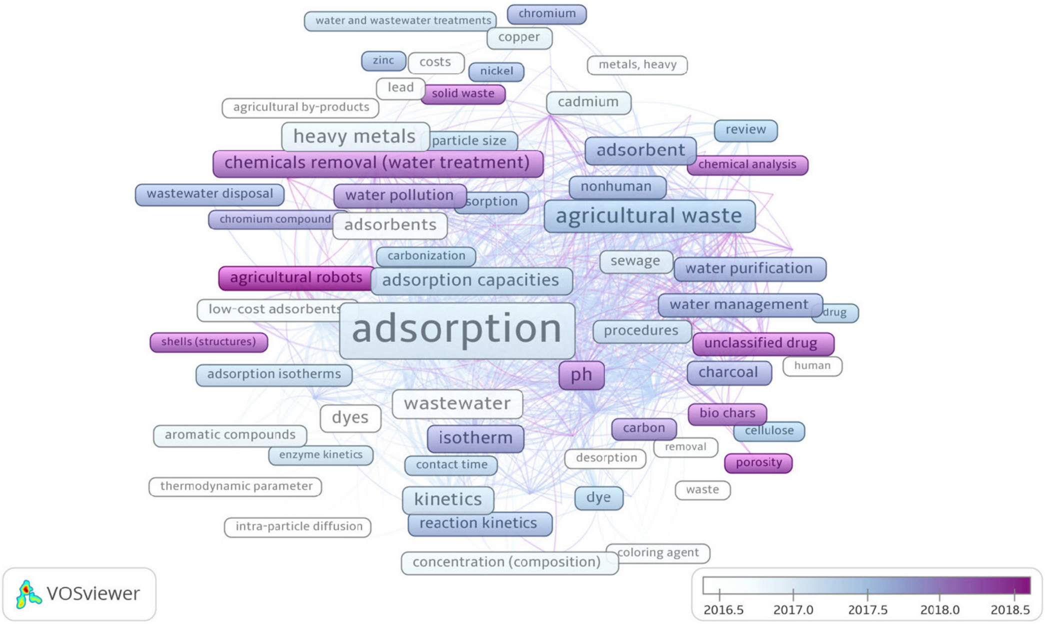

Figure 5. Keywords used by the authors in articles on adsorbents made from agricultural waste for use in effluent treatment in the period between 2010 and 2020.

Figure 6. Keywords used by the authors in articles about adsorbents made from agricultural waste for use in effluent treatment in the years 2021 and 2022.

covering all decades. It is important to note that, of the five most cited articles, four are literature reviews.

In the Scopus database, only 6 works published by Brazilian authors are found. The details of these articles, such as title, authorship, year of publication, journal and number of citations are presented in Table 2. Figure 7 presents the collaboration network between countries established by the authors of the six articles.

3. Synthesis and Characterization Techniques of Adsorbents from Agricultural Raw Materials

3.1. Production methods

Affording materials from natural sources to manufacture adsorbents might be difficult due to the lack of selectivity towards pollutant specificities, which exhibit surface

Table 1. Articles on adsorbents made from agricultural residues for use in effluent treatment most cited by other authors

Title	Reference	Year	Journal	Citations
Non-conventional low-cost adsorbents for dye removal: A review	32	2006	*Bioresource Technology*	3508
Application of low-cost adsorbents for dye removal - A review	33	2009	*Journal of Environmental Management*	2851
Adsorption of methylene blue on low-cost adsorbents: A review	35	2010	*Journal of Hazardous Materials*	2248
Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse - An agricultural waste	30	2002	*Water Research*	1024
Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review	41	2018	*Ecotoxicology and Environmental Safety*	866

Table 2. Articles on adsorbents made from agricultural waste for use in effluent treatment published by Brazilian authors

Title	Reference	Year	Journal	Citations
Removal of Methylene Blue from an Aqueous Medium Using Atemoya Peel as a Low-cost Adsorbent	48	2021	*Water, Air, and Soil Pollution*	2
Investigation of Citrus reticulata peels as an efficient and low-cost adsorbent for the removal of safranin orange dye	49	2021	*Environmental Technology (United Kingdom)*	9
Potential of agricultural and agroindustrial wastes as adsorbent materials of toxic heavy metals: A review	50	2020	*Desalination and Water Treatment*	6
Agricultural biomass/waste as adsorbents for toxic metal decontamination of aqueous solutions	51	2019	*Journal of Molecular Liquids*	96
Evaluation of two different carriers in the biodegradation process of an azo dye 09 Engineering 0907 Environmental Engineering	16	2019	*Journal of Environmental Health Science and Engineering*	3
Efficient mercury removal from wastewater by pistachio wood wastes-derived activated carbon prepared by chemical activation using a novel activating agent	52	2018	Journal of Environmental Management	81

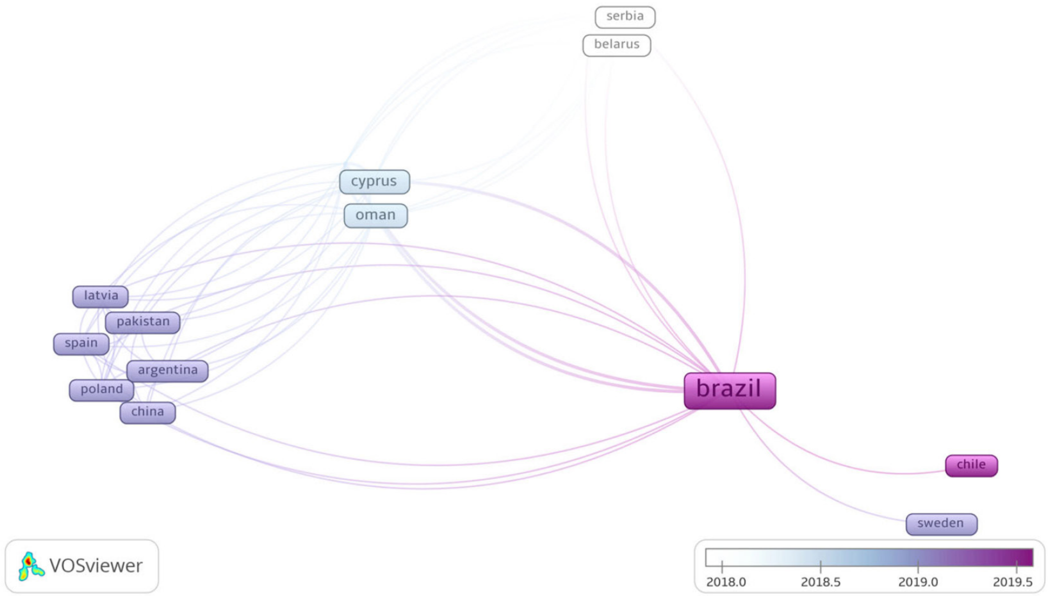

Figure 7. Collaboration network between countries in articles on adsorbents made from agricultural residues for use in effluent treatment published by Brazilian authors.

functionalities of diverse types of molecules.[53] This practice, however, has expanded, mainly because several biomass-derived adsorbents present competitive adsorptive capacities, when compared to synthetic commercial products, because they are readily available, are morphologically advantageous and usually exempt pre-treatments, making their use not only practical but highly cost-effective.[54]

Thus, depending on the source of biomass, proposed use and number of pollutants to be removed, these materials can be directly employed in their natural forms,[55,56] or subjected to physical-chemical pre-treatments.[57] An example is active carbon, the most common adsorbent, which still presents difficulties in industrial applications in the wastewater treatment due to the inflated cost of the synthesis. On the other hand, production of biochar poses as an economically feasible alternative, especially considering the low emissions of GHG.[58] Taking that into account and bearing in mind the scenario of the main Brazilian agribusiness cultures suitable for adsorbent production, henceforth we present the central processes used in the manufacture of adsorbents:

3.1.1. Pyrolysis

Currently, pyrolysis is one of the most widespread methods in the literature[59] due to the versatility in transforming diverse lignocellulosic biomass through thermal decomposition using temperature gradient under inert atmosphere, producing: a carbon-rich residual solid rich named biochar; an organic liquid product made of water, acids, alcohols, aldehydes, ketones, esters, phenols and aromatic compounds known as bio-oil; and gas mixture formed by moisture, H_2, CO, CO_2, CH_4, which can also be used as energy sources.[60]

Several authors have analysed pyrolysis process parameters to produce biochar, including temperature and decomposition time.[61-63] In general terms, temperature determines the degree of decomposition and carbonaceous content of the final charcoal, bio-oil and biogas products, and its raise may lead to higher contents in inorganic matter from the original raw material, and the formation of ashes.[60] Pyrolytic reactions are divided in: primary, generating products though the heat of biomass; secondary, which originate from the conversion of primary products; and tertiary, coming from the degradation of the last step products.[64] In addition, temperature directly influences the overall process cost, indication that, although low temperature might not provide a top-notch biochar, when too much heat is applied the reaction yield tends to be reduced and that restrains large scale production.[65]

Time of pyrolysis, in turn, sorts it in fast, when there is a short gas residence time (few seconds), which essentially produces bio-oil, and slow, aiming to form biochar, where the lignocellulosic biomass is processed for hours.[66] Under temperatures ranging from 200 and 600 ºC, it is possible to decompose raw material raising the degree of carbonization and pH of carbon content, while removing hydrogen, oxygen, nitrogen, and sulphate.[67]

Using this methodology, many cultures are being assessed to generate porous structures to be used in contaminated water treatment. Interest in corn cob, due to the porous macroscopic structure and shortage of industrial applications, directed mainly to animal food, stimulate the search for sustainable adsorbents. Authors subjected the previously washed and dried cobs to pyrolysis at 550 ºC under N_2 atmosphere for 2 hours, yielding a biochar that, although presenting relatively low surface area (8.99 m²/g), was able to adsorb up to 95% of heavy metals (lead and cadmium) at concentrations of 0.95 to 1.95 mg/mL. [68]

Synthesized biochar from coffee grounds using pyrolysis at different temperatures (400, 600 and 800 ºC) for 4 hours, obtaining an adsorbent material capable to quantitively remove perfluorooctane sulfonate (PFOS).[69] Produced biochar through slow pyrolysis, 2 h, at 450 ºC, from agriculture biomass – soy, corn and rice straw – to remove the herbicide atrazine, which is extensively used in pest control. The authors obtained materials bearing surface areas ranging from 17.5 and 25.8 m^2/g, pore volumes from 0.08 to 1.19 cm^3/g and alkaline pH, reaching adsorptive capacities up to 3 mg/g of pollutant.[70]

Produced biochar from sugarcane bagasse, through slow pyrolysis (400 and 600 ºC), to adsorb phosphate from an aqueous solution. The materials showed specific surface areas of 1.1028 and 1.8623 m^2/g and reach 15 mg/g of adsorptive capacity. Authors added chitosan to the bagasse biochar surface (1:1), amounting to removal values of 20 mg/g with twice the specific surface area.[71]

Wheat is another popular culture regarding the application of pyrolysis to develop biochar for adsorption processes. Authors made biochar using slow pyrolysis (300 to 600 ºC) and applied it to removal of heavy metal in contaminated water, achieving removals of 3.56 and 5.85 mg/g of mercury. The best results were accomplished using lower temperatures.[72] Researchers studied the production of biochar, also by slow pyrolysis, to remove Cd (II), using five different plant raw materials: corn straw, cotton, wheat, rice and poplar. Authors obtained high surface materials under a carbonization temperature of 600 ºC, varying from 37.7 m^2/g with poplar biochar to 183.3 m^2/g with wheat biochar, reaching adsorptive capacities of up to 500 mmol/kg.[73]

3.1.2. Hydrothermal synthesis

Recent hydrothermal processes used to synthesize biochar, or hydrochar as they are known, have fomented interest of various researchers on the grounds of being a low-cost and environmentally friendly technology, since it does not release hazardous gas in the atmosphere.[74,75] In this method, carbonaceous raw material is applied to a sealed reactor, which is heated to temperatures varying from 150 to 350 ºC for up to 12 hours under 10 MPa of pressure (Román *et al.*, 2016)[76]. Heating and pressure within the system generate a series of reactions, e.g., hydrolysis, dehydration, decarboxylation, demethanization and aromatization,[77] which, compared to conventional pyrolysis, yield materials with higher carbon and oxygen content, presence of well-defined pores and acidic pH, at the range of 3 to 5.[78,79]

The hydrothermal process is mainly influenced by the nature of the carbonized biomass, water content and temperature. High water content may accelerate carbonization, low temperature promotes the formation of biochar and steep heat favours the production of liquid and gas.[80]

A great deal of industrial crops residues has already been used as raw materials for biochar hydrothermal synthesis, by evaluation of the combustion effects in the wheat straw biochar synthesis and observed that as temperature and pressure rise, hemicellulose content gradually diminishes, especially from 180 ºC. For cellulose, as a result of the crystal structure, degradation does not start until 220 ºC, whereas lignin content rose from this temperature forth, and also, starting at this temperature up to 260 ºC, carbon microspheres begin to form on what was left of the biomass.[81] In a study showing the application of hydrothermal synthesis to coconut peat and husk, egg shells, rice husk and lemon at 200 ºC for 20 hours, authors managed to assemble highly porous adsorbents, with surface areas between 2.14 m^2/g for coconut peat, to 21.8 m^2/g for its shell. Compared to materials in their natural form, there was a significant increment, since their specific surface areas ranged from 0.09 to 1.23.[82]

Authors compared the efficiency of sugarcane bagasse *in natura* and transformed in hydrochar in recovering phosphate from aqueous medium. The charcoal was synthesized at 230 ºC for 1 hour, and the authors observed that carbonization opened pores on the structures which increase the phosphate removal by the 30% increase in removal related to *in natura*.[83] Less common residues were also evaluated, cassava husk hydrochar, for instance, showed a removal of the dye rhodamine B reaching 96%.[75] A collection of the most employed biomasses will be shown later on this work.

3.1.3. Treatments and activations

To achieve the necessary attributes that allow high adsorption yields in aqueous systems, materials require treatments aiming to improve both structural and functional properties.[84] This type of process, commonly known as pre-treatments or structural activation, removes unorganized carbonaceous structures, exposes lignin moieties to react with the activator, then interact with the porous walls, enhancing, in the first step, the mesoporosity of the material and in the second, its macroporosity.[85]

Acid treatments are applied to the crude biomass when one focus on functional alterations in hydroxyl groups, esters and carboxylic acids which compose the natural raw material, because the low pH will reduce lignin content and break bonds between cellulose and hemicellulose, also lowering crystallinity until the material becomes amorphous.[86] The resulting effect in general is an enhancement in surface area and pore diameter, as observed authors who treated rice husk with H_3PO_4 and used it to adsorb Cu (II). Microscopy images identified a significant pore enlargement, and infrared spectroscopy showed the presence of intense –COOH and –OH stretches, suggesting the exposure of the cellulose nucleus. These changes lead to 17.03 mg/g of adsorption capacity and 89% removal.[67]

The aforementioned treatments, when applied to charcoal and biochar are named activating, as employed by authors Piriya *et al.* (2021), who manufactured biochar from coconut shells through slow pyrolysis, and promoted a sequential acidic activation with H_2SO_4 e H_3PO_4, leading to a porosity enhancement from 19.19 to 49.02%. The authors deduced this improvement is due to the spike in number of carboxyl, phenol and hydroxyl groups.[87]

When the alkaline approach is the choice, natural carbonaceous materials have their morphological structure altered through lysis of lignocellulose, hemicellulose hydrolysis, lignin depolymerization and loss of fatty acids, which usually cover cellulose fibres, exposing their hydroxyl-rich core and increasing the adsorptive capacity of high-rugosity materials, enlarging the size of the pores and favouring electrostatic interaction between adsorbent and adsorbate.[88,89]

Sugarcane bagasse was chemically treated with NaOH to degrade lignin and expose cellulosic content and used it to adsorb the herbicide glyphosate from aqueous medium. The authors observed that the procedure heightened adsorptive capacity by nearly 35% and the rate of adsorption by over 60%, attesting the feasibility of the chemical process.[90]

Alkaline treatment (NaOH) was used on wheat straw biochar and compared it to acidic activations with HCl and HNO_3 to the same material. The alkaline treated material surpassed its acidic counterpart performance thanks to its large surface area and hydrophobicity, reaching removals of ofloxaxin, tetracyclin and bisphenol-A as high as 95%. Electrostatic and hydrophobic interaction and filling of pores mechanisms are responsible for these results.[91] Following this thread, other researchers developed rice husk biochar using KOH and obtained an adsorbent with a surface area of 1300 m^2/g, corroborating the influence of the alkaline activator to the efficiency of the biochar.[92]

Another way of chemical activation is the application of saline solutions ($ZnCl_2$, $FeCl_2$ etc) in order to reduce the temperature of thermal activation, focusing on the production of mesoporous biochar with high surface area.[93]

Thermal activations are prevalent amongst natural biomasses and their biochar, given that they only require the material be subjected to heat under oxidating atmosphere, which causes the enhancement of physical, chemical and mechanical properties, due mainly to the process conditions and the character of precursor biomass, being capable of altering the surface composition, water content and even granulometry.[94,95] For biochar, activating processes demand exposure to temperatures up to 700 ºC for hours to achieve the desired surface modifications.[96]

Biochar adsorbent was produced from wheat biomass using, amongst other techniques, thermal activation at

900 ºC, reaching six-fold increase in surface area and pore volume.[97] An absorbent from coffee grounds was synthesized through a thermal treatment aiming to adsorb diesel oil. The authors observed that heating the grounds to 300 ºC lead to increments in specific surface are, hydrophobicity, thermal stability, crystallinity, and adsorptive capacity to diesel of circa 50%.[98]

3.1.4. Natural Biomass

In face of the cost involved in conditioning, production and activation processes of natural adsorbents, many authors suggest the application of biomass as adsorbents without any previous treatments. [2,99] Besides the low cost linked to elevated availability, good selectivity to a number of pollutants, natural biomasses, especially those without inherent added value, become competitive related to commercial adsorbents.[100]

Residues from important agricultural cultures, cotton stalk among them were used to test their biosorbent abilities, without any pre-treatment, towards removal of heavy metals from water media, with positive results from lead and copper.[101] Recently, solely washed soybean husks were used to remove plantation field impurities, and subsequent drying and milling. The material was applied to remove reactive blue dye, with adsorptive potential of 53.33 mg/g and removal of 88%.[102]

Another recurrent Brazilian native residue, the cassava bagasse, was evaluated without pre-treatment, in the removal of scarlet red dye from water. Data showed a material with low surface area micropores (3.01 m^2/g), which, nevertheless, was able of removing 84% of the dye under acidic conditions with approximately 25 mg/g of adsorptive potential, putting this biomass among the promising sources for adsorbents.[103]

Sugarcane bagasse was also tested as adsorbent *in natura,* varying only the granulometry of the material. The structures obtained presented similar adsorptive capacities to methylene blue dye, close to 4 mg/g, regardless the initial concentration, reaching equilibrium between 5 and 7 hours. In this study, the authors indicate that sugarcane bagasse could be in a range of 20 to 45 mesh, with no significative difference in adsorption, hence, with a minute cost because of the reduction in processing times.[104]

Although the large-scale application seems yet far in the future, popularization of biosorbents in natura have augmented, largely because several agriculture residues have demonstrated potential adsorptive characteristics, added to the sustainable and environmental appeal that the correct use of this sort of material promotes.[105]

3.2. Characterization of natural adsorbents

In order to assure properties befitting the application of an adsorbent, it is necessary to subject the pre-treated materials, or yet, the natural biomass to characterization measurements, to seek the identification of structural and functional elements required to attest that the material might be an adsorbent,[106] and to what kind of pollutant they would efficiently interact with. The nature of these interactions rises great interest in the field, since the mechanistical explanations are responsible for extrapolating the use of these products to other contaminated water scenarios, including multiple component matrices of pollutants.[105]

On the subject of adsorbents of natural origin from agricultural crops, analyses might show characteristic elements pertinent to this class, and, depending on the treatment that the biomass received, one can observe specific parameters that will help to identify if said treatment was the driving motor to arrive at these characteristics. Among the frequently methods applied in material characterization, it is possible to highlight the most relevant:

3.2.1. Scanning Electron Microscopy (SEM)

This is technique features among the most widely explored to access solid surface, morphology and shape, and, to adsorption, it allows the elucidation of the adsorbent structures in terms of particle shape and size, presence and organization of pores and rugosity, i.e., elements that contribute to filling and adhesion of particles in the surface.[2]

For agriculture-derived materials in their natural forms, it is possible to stablish structural common patterns of interstitial layers, fibre arrangements, high rugosity amorphous granules, and pores distributed over several sizes.[107] Authors have compared scanning electron micrographs of corn straw before (Figure 8a) and after activation with HCl (Figure 8b). The acid promoted a surface decomposition, fomenting the opening of cavities with an average diameter of 10 μm, which is auspicious for adsorption processes.[108]

Jawad *et al.* (2020)[109] also used SEM to observe the structural alterations to corn straw biomass caused by acidic activation. However, in addition to identifying the pore opening after activation (Figure 9a), they noted, in the micrographs of the material after the adsorptive process (Figure 9b), a complete closure of the pores, suggesting a complete material covering and an elevated morphological influence in the adsorption.

Other authors have evaluated surface properties of natural biomasses using SEM, as done by Frollini *et al.* (2013),[110] who analysed structures of sugarcane bagasse, showing this material has a surface organized in hemicellulose bundles with a cellulosic interior arranged in hollow tubular structures with variable diameters. Chen *et al.* (2013) identified accumulated lamellar structures form the walls of wheat and maize straw, with a capillary framework within the lamellas that might actively contribute to adsorption.[111]

In the form of biochar, authors have indicated that such materials tend to form different rugosity degrees. When subjected to activation processes, there are usually hemicellulose residues clustered within the pores, accumulation gradients of residues, and larger specific surface areas and wider pores.[83]

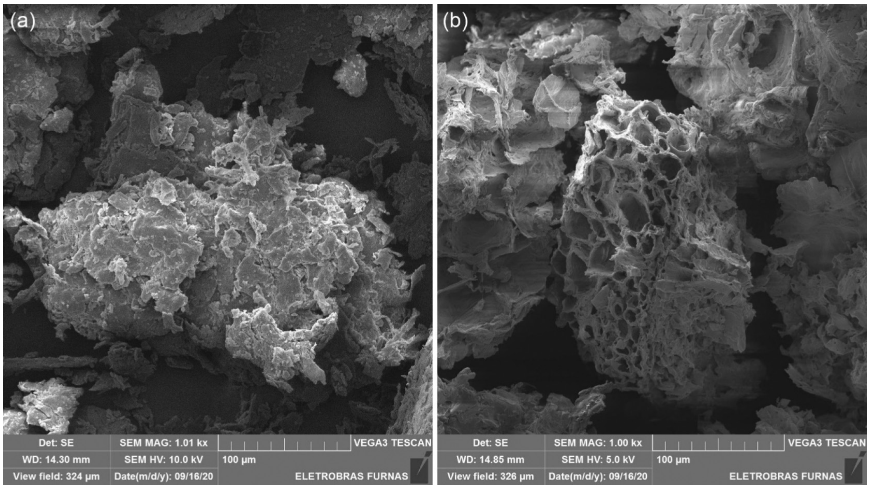

Figure 8. (a) SEM of corn straw without pre-treatments; (b) SEM of corn straw treated with HCl.[108]

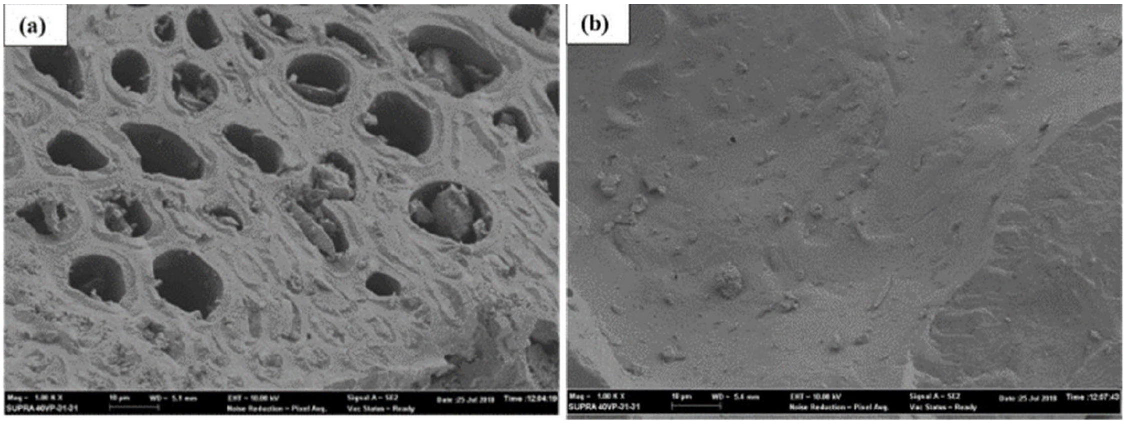

Figure 9. (a) SEM of corn straw treated with H_3PO_4; (b) SEM of corn straw treated with H_3PO_4 covered with methylene blue dye after the adsorptive process. [109]

3.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

From the molecular vibration response after being blasted with radiation in the infrared frequency, it is possible to obtain a functional groups signature of the adsorbent surface, aiding to identify likely mechanisms of interaction between materials and pollutants. According to Furlan *et al.* (2008), who evaluated IR spectra of corn, wheat and soybean straws, in natural biomass there is nearly a standard spectrum to be expected, constituted of OH stretches (3100-3500 cm^{-1}) from moisture and interstitial water content, C=O signals around 1633 cm^{-1}, O-C-O at 1400 cm^{-1} and C-O-C at 1045 cm^{-1}, representing the cellulosic structure.[112]

Golveia *et al.* (2021) evaluated corn stalk and identified OH stretches at 3000-3700 cm^{-1} and C-C-C bends at 1100-850 cm^{-1}, proving the cellulosic nature of the material and suggesting favourable interactions with polar pollutants.[108] Kamsonlian *et al.* (2012) showed similar functional groups in banana peels.[113]

Thawornchaisit *et al.* (2021) worked with raw sugarcane bagasse, and biochar from the same biomass, and show the existence of hydroxyl groups from moisture and Csp3-H stretches, suggesting the presence of aliphatic compounds. Carbonyl groups, pointing out to hemicellulose, appeared only in the crude bagasse, which is expected in face of the thermal degradation that takes place during carbonization. At the 1100 to 1500 cm^{-1} range, where cellulosic and aromatic signals can be found, only biochar showed vibrational signals, confirming the exposure of cellulosic core of the material.[83]

Mariana *et al.* (2018) used FTIR analyses of coffee bean residues *in natura* and after acid activation with HCl. The authors identified Csp3-H groups at 2905 cm^{-1}, OH and carboxylic acids with a large band between 3550 and 2400 cm^{-1} and C=O from esters at 1755 cm^{-1}. Prominent C=O and COOH stretches suggest the acid treatment degraded the hemicellulose, exposing lignin and cellulose.[114] Similarly, Guo *et al.* (2016) observed that when wheat straw is treated with an alkali (e.g., NaOH) C-O stretches were augmented, leading to an increase in Cu (II) adsorption through interaction with ether groups.[115]

In the same field, Souza *et al.* (2021) also evaluated FTIR spectra of biochar from açaí seeds. The biochar samples were activated via acid (H_3PO_4) or alkaline (NaOH) processes. The result suggested that both treatments remove vibrational bands at 1773, 1685, 1570 and 143 cm^{-1}, which represent the decomposition of oxygenated moieties within cellulose and hemicellulose. FTIR data also indicated the presence of acids, phenols, ethers and esters, once again pointing to an exposure of the cellulosic matrix post-treatment. In addition, functional groups bearing phosphorous were also present in the H_3PO_4 product, e.g., the P=O stretch at 1261 cm^{-1}. The authors have shown that treated açaí biochar has a predominantly acidic surface, favouring the adsorption of pollutants with an alkaline character.[116]

3.2.3. X-Ray Diffraction (XRD)

According to Anirudham and Unnithan (2007), X-ray diffractogram of natural adsorbents of cellulosic character, exemplified by their studies with coconut fibres, essentially correspond the presence of scattered angles at 21.2°, 38.2° e 43.5°, representing an orderly array of cellulose molecules.[117]

Similar patterns were observed by Ajala *et al.* (2022) when they evaluated sugarcane bagasse both *in natura* and chemically treated as adsorbents. Characteristic peaks were measured at 14°, 21° and 28°, with a higher intensity for the 21° signal, indicating the unfolding of the cellulosic structure in a crystalline material.[118] Harripersadth *et al.* (2020), studying the same biomass, encountered peaks at the 22° range referents to native cellulose with plane (002) present. The authors, however, demonstrate that the presence of lignin, an amorphous material bound to cellulose, reduces the intensity, or withdraw the sharp form of peaks of the biomass.[119] Jawad *et al.* (2018) evaluated banana peel and detected peaks at 24° (002) and 42° (101), indicating this biomass presents an analogous cellulosic crystalline structure.[120]

Biochar adsorbents are usually formed of amorphous structures and their diffractogram do not show well-defined peaks, they show though broad bands in the 2θ region between 22 and 25°,[109] due to the remains of cellulose not degraded during the thermal process. A similar pattern was assessed by Papala *et al.* (2021),[121] who produced biochar from rice husk and identified a large reflexion peak at 2θ = 23° (002), related to the biomass *in natura*, which formed a sharper and closed peak (2θ = 23° (002), suggesting the degradation effect the biochar production brings about, becoming more amorphous due to the lignin residual content. Karami *et al.* (2022) identified 2θ = 22-28° and 2θ = 42° for biochar from corn stalks, suggesting an amorphous carbon structure formed by C_6-C_{60} e graphite befitting the scorching temperature applied to producing this biochar.[97]

3.2.4. Thermal analysis

Thermogravimetry, (TG) with Derivative Thermogravimetric analysis (DTG), and Differential Scanning Calorimetry (DSC) are the most prevalent thermal analyses. Golveia *et al.* (2021), working with corn stalk residues, observed, using thermogravimetry, that lignocellulosic materials tend to have three mass loss stages. TG and DTG both indicate that the mass loss at 100 ºC is mainly associated with free water enclosed in the crop-derived material. Hemicellulose decomposes at around 275 ºC and cellulose, which presents higher heat resistance, starts decomposing at 300 ºC. Through DSC analysis, Golveia *et al.* (2021) also observed an exothermic spike that start at 350 ºC and peaks at 450 ºC.[108]

Vieira *et al.* (2012) analysed natural and thermally activated (calcination) rice husks as adsorbents. TG/DTG measurements suggested a mass loss of 6% between 48 and 90 ºC, indicating the presence of volatiles and water in the system, and another loss of 54% at 350 ºC – degradation of hemicellulose and most of cellulose. Finally, at approximately 600 ºC, lignin starts decomposing until there is nothing but ashes. Calcinated samples showed mass losses of only 2.5% from 25 to 150 ºC, referent to the remaining free water – which was expected since the volatiles and most of the water were removed during thermal treatment – and another 22% mass reduction due to interstitial water and then carbonization. DSC analyses of rice husk showed energy absorptions at 77 ºC and 300 ºC, implying the evaporation of volatile and non-volatile organic compounds, respectively.[122]

Other farming cultures also exhibited similar thermal behaviours. Awokoya *et al.* (2016) evaluated the cassava husk structure, noticing 5% of mass loss until 100 ºC, but a surprising 80% loss from 300 to 390 ºC, due to the degradation of carboxylic compounds.[123] And Verma *et al.* (2021), working with coconut shell residues, likewise observed an 80% mass loss from 170 and 415 ºC, denoting in both cases that lignocellulosic composition of the material determines the rate of mass loss within the cited ranges. In Verma and co-workers' (2021) case, the adsorbent lost 3% of hemicellulose, 54% of cellulose and 30% of lignin from 170 to 415 ºC. And, as expected, hemicellulose degraded first, followed by cellulose and, lastly, lignin decomposed.[124]

3.2.5. Adsorption-desorption of Nitrogen at 77 k

Adsorption-desorption of N_2 at 77 helps to identify the porous character of a system, as well as to calculate the surface area and porous volume and diameter, alongside with BET and BJH techniques.[73] Regarding adsorbents from agricultural biomass, Bavaresco *et al.* (2021) observed that corn straw bears a low surface specific area when in the natural form, 2.662 m^2/g, and has a mesoporous structure with total pore volume of 0.0066 cm^3/g. After thermal activation via calcination, on the other hand, the authors showed both surface area (109.4 m^2/g) and porous volume (0.075 cm^3/g) enhancements, becoming more competitive against commercially available active carbons.[107] Surface areas and porous volume in biochar are inversely proportional to the lignin content in the precursor biomass, corroborating the previous data that show the deterioration of lignin during activation or carbonization might improve the adsorbent character of agrarian residual material. Table 3 shows a collection of surface areas of different crops and their biochar applied to adsorptive processes.[73]

Table 3. Surface area and porous volume of adsorbent materials from agrarian origin

Culture	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Reference
Soybean Husk	< 1	-	125
Soybean Biochar	1425-1620	0.638-0.751	126
Corn Stalk	1.22	-	127
Corn Stalk Biochar	407	0.155	128
Coffee Grounds	0.19	-	129
Coffee Grounds Biochar	388.4 - 987.9	0.528-0.984	130
Rice Husk	1.4	-	122
Rice Husk Biochar	13.6	0.0076	131
Cassava Husk	2.051	0.002233	132
Cassava Stem Biochar	6.882 - 9.4964	0.00237 - 0.00247	133
Beans	179.1	0.036	134
Bean Biochar	-	-	-
Banana Peel	3.089	0.004977	132
Banana Peel Biochar	1.2 - 7.5	-	135
Wheat Straw	4.6 - 5.9	0.745	136
Wheat Straw Biochar	15.8	-	137
Coconut Fibre	38.84	0.436	138
Coconut Fibre Biochar	331.86-811.46	-	139
Açaí	-	-	-
Açaí Seed Biochar	1.94 - 491.90	0.003 - 0.315	140
Cocoa Husk	0.021	-	141
Cocoa Husk Biochar	118 - 502	0.09-0.50	142
Manga Peel	13.455	0.055	143
Manga Peel Biochar	2.09 - 5.74	0.00183 - 0.00366	144

The data shown in Table 1 are a sign of the viability of adsorptive application of natural biomass from agricultural origin, considering their porous structures, especially biochar. These products are competitive facing commercial active carbons, since they have specific surface areas at the range of 1500-2000 m^2/g and porous volumes around 0.7 cm^3/g,[145] making the materials not only economically viable related to the cost of traditional active carbons, but also readily available.

4. Adsorbents Produced using Important Crops from Brazilian Agribusiness

Agribusiness market moves billions of dollars a year – Brazilian 2021 harvest alone generated a revenue of R$ 651.75 bi (IBGE, 2021)[146] – besides creating jobs and strengthening the economy, especially in the poorest regions of the country. Out of this number, 83.4% are owed to ten cultures: soy, wheat, sugarcane, coffee, cotton, rice, orange, cassava, beans and banana. Besides these, based on the 2021 harvest data (Table 4), wheat, coconut, açaí, mango and cocoa cultures are prominent amongst the national crops.[147]

Planted areas and quantities harvested of the cultures highlighted above (Table 4) draw attention to a factor that largely impacts the economy and, withal, the environment: the number of solid residues generated during and after harvesting these vegetables.

Taking soybean as an example, despite the absence of continuous data collection on the tonnage of residues produced every year, one can use the harvest index (HI = mass of grain produced over total dry mass of the plant) to suggest the quantity of "garbage" left at the end of the season. In a recent work, Jiang and co-workers (2019) found HI values between 0.14 and 0.60, averaged at 0.42 for soybeans cultivated in the Northeast of China. If Brazilian agriculture yields a similar index, the bulk of solid waste here would be around 321 million tons.[148]

This alarming number supply of material should not simply be discarded in the environment. For some important cultures, the wastes are already reused within the agroindustry itself. Sugarcane, for instance, is widely used as source for bioenergy and biomaterials.[149-151] There are yet abundant biomass that goes to waste in the agrarian sector. This plant-based biomass, constituted mainly of lignocellulose and hemicellulose as already discussed, may be sustainably utilized to develop high-value products, among which, feature the biosorbents.[152]

The following topics discuss the major types of adsorbents produced using some of the most important Brazilian agricultural crops – soy, corn, coffee, rice, cassava, beans, banana, wheat, coconut, açaí, coca and manga – and their application in wastewater treatment.

Table 4. Numbers of planted area, quantity harvested (in tons) and revenue of some of the main Brazilian agricultural crops during the 2021 harvest

Culture	Planted Area (Hectare)	Harvest (Tons)	Revenue (Millions Reais)
Soy	39,185,745	134,934,935	341,747,600
Corn	19,587,069	88,461,943	116,396,867
Coffee	1,836,741	2,993,780	34,896,546
Rice	1,689,189	11,660,603	19,146,736
Cassava	1,205,829	18,098,115	12,702,124
Beans	2,613,086	2,899,864	12,049,373
Banana	453,273	6,811,374	9,998,070
Wheat	2,750,264	7,874,525	10,998,648
Coconut	186,392	1,638,573*	1,299,188
Açaí	208,111	1,485,113	5,305,523
Cocoa	600,789	302,157	3,973,400
Mango	76,061	1,505,372	1,953,638

Source: IBGE - https://www.ibge.gov.br/explica/. roducao-agropecuaria/. *Quantity of fruit

4.1. Soy

Soy is the second Brazilian agrarian commodity in terms of quantity of residues generated, surpassed only by sugarcane.[153] Grain husk and the straw are the main source for adsorbent materials obtained from this culture. The straw, a lignocellulosic material originating at the stalk, is abundant and unexpensive, but, due to their low-nutritional value, it is frequently discarded or burnt. The husk, on the other hand, corresponding to 8-10% of the total mass of grain, is a by-product of plant processing, especially for oleochemistry industry.[154]

Soy straw has a surface teeming with pores of various sizes, with opening diameters ranging from nanometres to micrometres. This allows, for adsorbents produced with this biomass, the adsorption of molecules, being organic or inorganic (e.g., metals) in different regions of the material.[154]

Pyrolysis stands out as a method to produce adsorbents from soy straw. Several examples of soy biochar can be found in the literature being used to treat effluents containing textile dyes,[155] basic and anionic compounds[156] and metallic cations, such as chromium[157] and cadmium[158]. Products from this plant matrix are not limited to biochar, straw – both *in natura* and chemically treated – have been used in the treatment of effluents rich in Cu^{2+}[154] and the active carbon – activated with $ZnCl_2$ – of the same source was efficient in the treatment of coloured effluents.[159]

Soybean husk is, however, underused. Despite the high quantity of polysaccharides, especially cellulose, only around 10% of the husk is destined to animal nutrition, a great deal of the overplus ends being discarded or incinerated.[160] This plant possesses interesting characteristics – dilation capacity, porosity, surface area – that concomitantly favours the adsorption of molecules both hydrophobic and hydrophilic.[161]

The main effluents treated with soybean husk adsorbents originated from the pharmaceutical and, principally, textile industries. Recent studies have demonstrated the efficacy of this biomass when applied to the remediation of residual waters contaminated with hormones,[162] non-steroidal anti-inflammatories[160] and antibiotics. [163]

Dyes are also important pollutants, prevalent in diverse industries. Beyond the obvious role in textile factories, they are widely explored in the production of plastics, paper, medicines, and cosmetics, to cite only a few, which consume enormous volumes of water, generating vast quantities of coloured effluents.[164] Soybean husk products are being extensively studied as suitable agents to address this issue. The list of dyes treated is ample, but we can point out the use of this biomass to adsorb direct red 80 and 81, acid blue 92 and acid red 14,[165] safranin T, Remazol brilliant blue and direct violet 51,[166] reactive yellow 145 and reactive blue 21,[161] methylene blue[164] and reactive red 4B.[167]

4.2. Corn

With a revenue of over 116billion reais in the 2021 harvest,[146] corn ranks second among Brazilian cultures that generate wealth in the country, surpassed only by soy. A cornerstone for this result is the impressive adaptability of this crop to the most diverse climate conditions: maize is cultivated from south to north, in both humid and arid regions.[168]

Residues assembled from different corn parts are employed in the production of adsorbents, the more fruitful are the: cob, stalk, straw and bract. The active carbon manufactured from corn cob proved to be a versatile material, it was suitable for removing metals from water in lab-scale tests,[169,170] in addition to being successfully used to treat effluents containing amino acids[171] and dyes.[172] The cob is also a source for nanocomposites which demonstrated high adsorptive capacity for metals, such as lead[173] and cadmium.[174]

Corn stalk is another waste product of the maize industry produced in exuberant amount. It is constituted mainly of cellulose, hemicellulose, lignin and SiO_2,[175] which makes it attractive as a source of adsorbents. Products made from the stalk have been applied to the remediation of metal solutions, both *in natura*, to adsorb Pb (II),[176] and modified with amines, to remove Cr (VI)[177] and Cd (II).[178] Biochar derived of the same biomass presented remarkable results in remediation of coloured effluents[179] and ionic liquids.[175]

Likewise, corn straw is also a rich biomass source commonly incinerated and, generally underused.[180] Straw structure is irregular and porous, with large surface area, favouring the physical adsorption of pollutants. Its chemical composition is rich in carbohydrates, lignin and proteins, with an elevated ion coordination capacity.[111] The combination of these characteristics boosts the efficiency in the adsorption of organic – green malachite dye,[180] ethers and benzene[181] and atrazine[182] – and inorganic compounds – cations such as Cr^{3+} and Cr^{6+}.[111]

4.3. Coffee

Coffee is one of the most consumed beverages in the world. The culture, which has a central role in Brazilian history and politics for the past three centuries, continues to be lucrative to farmers, raising almost 35 billion reais in the 2021 harvest.[146] Nonetheless, with the rise of worldwide production, there a proportional increase in residues. The main remnant products of the coffee industry are the grounds, silverskin and husk.[183]

Coffee grounds is a small-sized particulate residue, high in moisture and organic content, mildly acidic, obtained after preparing coffee.[183] Colossal amounts of grounds are discarded per year, the residue mass corresponds to approximately 65% of grain.[184]

Adsorbents synthesized using coffee grounds as source material are applied to the remediation of a diverse group of effluent, since long-stablished contaminants, such as pharmaceuticals[184-186] and metallic cations[187] to complex mixture of organic remains, found in mine leachates[188] and landfills.[189]

Silverskin is a by-product of the coffee beans roasting. This fine membrane which covers the grain comes off during the heating process and is the only by-product originated at this stage of the productive chain. Its structure is predominantly constituted of food fibre – rich in carbohydrates –, proteins and a few minerals. The inadequate disposal of this biomass causes serious environmental problems: silverskin has a high content of methylxanthines, polyphenols and tannins, which renders an elevated phytotoxicity.[183,190]

The use of silveskin as adsorbent is recent, but it has increasingly attracted attention in the last decade. Ismail and co-workers (2017) have shown that silverskin nanoparticles are able to remediate used cooking oil.[191] And Pozo *et al.* (2021) used the biomass-derived biochar to treat coloured effluents.[190] The *in natura* product also presented high adsorptive capacity, when employed to remove Cu^{2+}, Zn^{2+}, Ni^{2+} [192] and Cr^{3+} e Cr^{6+} [193] from contaminated water.

Coffee husk, constituted of the external dry skin, pulp and parchment, is a major residue that remains after harvesting and processing of coffee, and makes up nearly 1/4 of the grain mass.[194] Husk-derived biochar is particular attractive. To obtain a good yield in the production of the biocharcoal it is crucial to collect a biomass rich in cellulose, lignins and ashes, these components represent 84% of the husk.[195]

Active carbon produced using coffee husk has been extensivily explored to treat coloured effluents, containing, e.g., methylene blue,[194,196] methyl violet and pararosaniline[197] and malachite green.[198] This sor of adsorbent is also able of removing íons from residual waters[199] and pharmaceuticals from biological samples.[200]

4.4. Rice

Brazilian production of rice in 2021 surpassed 11.6 million tons.[146] During the processing of this gigantic quantity of grains, the rice husk is commonly discarded. This product, which represents around 1/5 of its mass,[201] is comprised of around 20% of SiO_2,[202] making it a promising candidate as source for adsorbent materials.

This significant amount of silicon dioxide enables the synthesis of a type of adsorbent that is not usually produced from organic matter. Silica derived from rice, with and without the addition of iron, was used to remediate coloured effluents.[203] For the remediation of pharmaceuticals, Pham and co-workers (2021) synthesized hybrid nanoparticles (SiO_2 and CeO_2) and used them to remove amoxicillin from residual waters.[204]

Rice husk is largely employed to adsorb metals from water solutions. Materials manufacture from this part of the grain showed to be effective to adsorb Cu^{2+}, Al^{3+}, Ni^{2+} and Zn^{2+} and Pb^{2+}, Cu^{2+}, Cd^{2+}, in addition to binary mixtures of these cations.[201,205] The versatility of this biomass is not limited to inorganic ions: hydrolysed hush, straw and active carbon from rice are excellent adsorbents when applied to organic compounds, such as 2-nitrophenol,[206] the antibiotics azithromycin and erythromycin[207] and the analgesic paracetamol.[200]

4.5. Cassava

Cassava plan is a tubercle native of South America which is part of the diet of around 700 million people worldwide, especially in the developing countries. Brazilian harvest represents 10% of the global production.[5] Plantations are distributed for all states and the cultivation takes place at both massive estates and at small farms.

The culture yields colossal quantities of solid residues, principally throughout root processing. Among the generated wate, cassava peel has a notorious position, it constitutes 3 to 5% of the root weight,[208] which, considering the 2021 harvest,[146] leads to estimate ranging from 543 to 905 ton of peel produced only in Brazilian land.

The use of casava residues as raw material for adsorbents is novel, there are only a few groups working with this biomass. Despite that, the performance of the products already produced from the peel and the root bagasse foresees an auspicious future in the field, especially regarding the application in the treatment of effluents containing metallic cations, such as Cd^{2+}, Pb^{2+}, Cr^{3+} and Ni^{2+}.[208-210]

4.6. Beans

Beans are farmed in all five regions of the country. Brazil is the largest producer in the world, the 2021 harvest yielded over 12 billion reais.[146] Paraná, Minas Gerais and Bahia states have the most massive farms and produce circa of 50% of beans reaped in the national territory.[211]

After reaping and threshing the grain, around 60% of the plant becomes waste, and Brazil is responsible for 5.7 million tons of beans per year.[212] In an attempt to reduce the impact of the waste, and further obtain products with significant added value using materials that otherwise would be garbage, the bean pod and husk have been surveyed as precursors to the synthesis of adsorbents.

The number of studies reporting the use of this biomass *in natura* is modest, most likely because the crude material presents low adsorptive capacity.[212] Yet, Bayomie and co-workers (2020) showed that, under ultrasound assisted stirring, bean husk biomass in the natural state can remediate coloured effluents.[213] Besides that, the biochar, manufacture using both pod and husk, was successfully utilized to adsorb organic compounds, such as naphthalene and the dyes methyl orange, methylene blue, Congo red and malachite green.[214,215]

A fascinating alternative to amplify the biomass adsorptive capacity is the collection of chemical treatments previously discussed. Sá and co-workers (2022) showed that the acid activation of the bean pod with HNO_3 lead to a product with considerable affinity to fluorescein, a property which only aroused after the chemical treatment.[212] For the removal of inorganic compounds, Raulino and co-workers (2018) described a 45% increase in the removal rate of Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+} and Cd^{2+}, after the pod was subjected to an alkaline treatment followed by the addition of organic acids.[216]

4.7. Wheat

Wheat is one of the most consumed cereals in world. The culture represents 8% of all vegetable reaped on the planet and, with 800 million tons harvested, ranks fourth in worldwide production, behind sugarcane, corn and rice.[8] Wheat sales yielded nearly 11 billion reais in the 2021 Brazilian harvest.[146] The husk, straw and bran are main residues gathered during wheat harvesting and processing.[217,218]

The wastes of the wheat culture, quite similarly to the biomasses discussed so far, are comprised mainly of cellulose, hemicellulose, lignin and other carbohydrates.[218] Therefore, the methods used to prepare adsorbents detailed in the previous section also apply to this biomass.

Wheat husk, after acid activation with perchloric acid, showed remarkable adsorption properties to remediate coloured effluents.[219,220] The wheat straw and bran *in natura* originated products able to adsorb lead[221] and chromium.[111,222] The biochar produced with these biomasses also shows high adsorptive capacity towards metallic cations.[223,224]

Table 5 summarizes the different types of adsorbents produced using biomass residues accumulated after harvesting and processing of the main cultures of the Brazilian agribusiness.

5. Application in Real Wastewater Treatment and Perspectives

A great deal of new adsorbents is emerging in the last years, with special attention to reuse waste. Among the valuable wastes that can be used as adsorbents, agricultural residues have shown huge potential due its diversity, amount generated and specially regard to the features these natural materials. During the preparation of this work it was possible to notice that besides the high number of different materials been studied, still existing a lack of works applying these materials on real wastewater. Therefore, the authors want to point out the necessity to amplify the use o agricultural base materials and consequently stimulate the transference of the technology from lab scale to industrial applications. For this, it will be shown a group of results using the agricultural cultures presented above which were applied to real contaminated water.

For instance, in order to verify the efficiency of the soy waste biomass as adsorbent to remove heavy metals from water, Bulgariu and Bulgariu (2018) tested batch system and industrial wastewater from a printing company. The removal of Pb(II), Cu(II) and Ni(II) ions was investigated and an economical study was carried out. The authors have achieved a high removal potential and a lower cost compared with the precipitation method usually applied by the company.[225]

Additionally, Ma and co-workers (2019) transformed corn straw in a highly efficient porous adsorbent used to remove chromium (VI) from water. As can be seen on Figure 10, the thermal activation has transformed the waste material promoting the porous and revealing functional groups on the surface of the material that have chemical activity to attract and trap the pollutant studied. Figure 10. Preparation of the adsorbent and suggestion mechanism for chromium (VI) removal. It was observed a removal efficiency of 97.90%, even in presence of Fe^{2+}, Ni^{2+} and Cu^{2+}, no change was observed in the adsorption efficiency. These results indicated that although the existence of Fe^{2+} exhibits a competitive effect, the porous carbon adsorbent still presented excellent removal of Cr (VI) from electroplating wastewater.[226]

Table 5. Adsorbents produced using solid residues from the main Brazilian agricultural crops and the types of effluents they remediate

Culture	Part of the plant	Type of adsorbent	Effluents/residues treated	References
Soy	Straw	*In natur*a and Chemically activated Biochar/Active carbon	Cu^{2+} Methyl violet Ammonia, nitrate and phosphate Cr^{3+} Cd^{2+} Brilliant red K-2BP	154 155 156 157 158 159
	Husk	*In natura* and Chemically activated	Hormones Non-steroidal anti-inflammatories Antibiotics Dyes	162 160 163 165 166 161 164 167
Corn	Cob	Chemically activated Biochar/Active carbon	Pb^{2+} Cd^{2+} Cr^{6+} Amino acids Dyes Cu^{2+} e Ni^{2+}	173 174 169 171 172 170
	Stalk	*In natura* Chemically activated Biochar/Active carbon	Pb^{2+} Cr^{6+} Cd^{2} Dyes Ionic liquids	176 177 178 179 175
	Straw	*In natura* Chemically activated Biochar/Active carbon	Cr^{3+} e Cr^{6+} Dyes Methyl-t-butyl ether and benzene Atrazine	111 180 181 182
Coffee	Grounds	*In natura* Biochar/Active carbon Chemically activated	Mine leachate Cr^{6+} Tetracycline Balofloxacin Landfill leachate AAS, paracetamol e caffeine	188 187 186 184 189 185
	Silverskin	*In natura* Biochar/Active carbon Chemically activated	Cu^{2+}, Zn^{2+}, Ni^{2+} Cr^{3+} and Cr^{6+} Dyes Used cooking oil	192 193 190 191
	Husk	Biochar/Active carbon Chemically activated	Dyes NH_4^+ Paracetamol Dyes	194 197 199 200 198
Rice	Husk	Chemically activated Biochar/Active carbon Modified silica	Cu^{2+}, Al^{3+}, Ni^{2+} and Zn^{2+} Pb^{2+}, Cu^{2+}, Cd^{2+} 2-nitrophenol Paracetamol Azithromycin, Erythromycin Dyes Amoxicillin	201 205 206 200 207 203 204
Cassava	Husk	Chemically activated Biochar/Active carbon	Cd^{2+}, Pb^{2+}, Cr^{3+} Ni^{2+}	208 209 210
Beans	Pod	Chemically activated Biochar/Active carbon	Fluorescein Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+} Naphthalene	212 216 214
	Husk	*In natura* Biocar/Active carbon	Dyes Dyes	213 215
Wheat	Husk	Chemically activated	Dyes	219 220
	Straw	*In natura* Biochar/Charcoal	Cr^{3+} and Cr^{6+} Ni^{2+}	111 223
	Bran	*In natura* Biochar/Active carbon	Pb^{2+} Cr^{6+} Cr^{6+}	221 222 224

In this way, Lima and co-authors (2017) used ultrasound modified corn straw to remove malachite green removal from synthetic and real effluents. The application in real effluents composed of dye mixtures and inorganic compounds. The authors concluded that the ultrasound treatment turned the adsorbent in a more attractive material to remove the studied pollutants, by comparison with the raw material. The raw material and ultrasound modified adsorbent achieved removal percentages of 77 and 81%, respectively. Nevertheless, the most attractive result was found when the adsorbent was applied to treat textile effluents with a mixture of dyes and inorganic compounds, in which the color removal of 92% was achieved.[180]

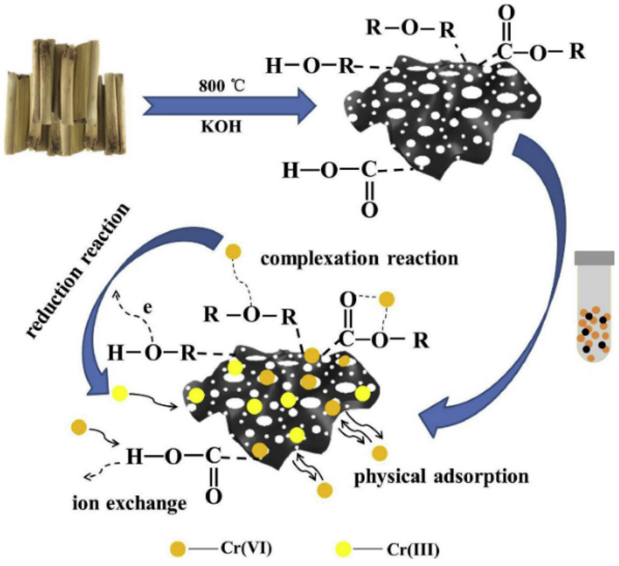

Figure 10. Preparation of the adsorbent and suggestion mechanism for chromium (VI) removal.[226]

Aditionally, Pathak and co-workers (2015) have applied rice husk ad adsorbent to treat dairy wastewater. Using an adsorbent dosage of 5 g/L, the authors achieved 92.5% removal at 30 °C, indicating a cost-effective process since it is cheaply available raw material. Thereby, the authors pointed that the use of the raw material without previous treatement could increase the COD load of the wastewater, because the silica on the outer and impurities (fats and waxes) on the inner surfaces cause improper binding between the active sites and molecules. Therefore, activation must me conducted to ensure higly efficiency of the adsorbent.[227]

Using spent coffee grounds activated carbon, Yuan and Ferraz (2020) applied the produced adsorbent to remove organic matter and color from synthetic and real landfill leachate. The authors activated the biomass with phosphoric acid at different ratios, tha material impregneted using the lowest acid ratio and pyrolysis temperature of 500 °C presented higher surface area. The activaded carbon produced achieved a COD removal of 40 mg per gram of adsorbent, the material showed excelente performance when real landfill leachate was used, reaching >90% of color and COD removal.[228] Follow this line, coffee husk was used to produce biochar by pyrolysis process without any activation process and used to remove ammonium in water and wastewater. The pyrolysis was carried out at low temperatures of 350 °C in a short time of 1 h. The adsorbent presented a relatively high adsorption capacity after 6 h with maximum 2.8 mg N/g biochar. The ammonium removal by coffee husk biochar could be reached the efficiency of 43% at 25 °C, initial ammonium concentration of 50 mg/L, and pH of 7. These findings are relevant to highlight that a worldwild culture as coffee can significantly improve the water and wastewater treatment in a social and economical way, since the coffee husk biochar produced from low temperature pyrolysis could substitute high-priced commercial adsorbent to treat ammonium from different water and wastewater sources.[229]

The capacity of biochars derived from agricultural wastes to remove Cd(II) and Cu(II) from aqueous solution and contaminated mine water was evaluated by Bandara and co-workers (2020). The authors produced biochar from different agricultural sources, for instance, poultry litter; lucerne shoot; vetch shoot; canola shoot; wheat straws; and sugar-gum wood. Afterwards, it was demonstrated that poultry litter-derived biochar removed Cd(II) and Cu(II) from mine water up to the levels recommended by the World Health Organisation. The experiments showed that precipitation with carbonate and phosphate, complexation with –OH and –COOH groups and electrostatic interaction with O-containing surface functional groups were the main mechanisms involved in the removal, as represented in Figure 11. This remarcks can drive the biomass selection to produce the biochar addressed to maximise remediation of multi-metals in contaminated water.[230]

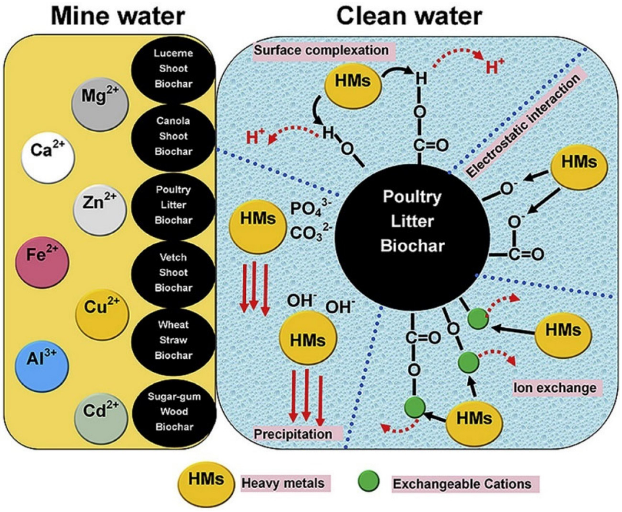

Figure 11. Different mechanisms involved on metals removal from water and wastewater.[230]

Talking about mechanism, it was determined that cassava waste consists of ligands such as hydroxyl, sulfur, cyano, and amino which could bind heavy metal ions. Abia and co-authors (2003) conducted a study stablishing the optimal concentration of thioglycolic acid for the removal of Cd^{2+}, Cu^{2+}, and Zn^{2+} ions by cassava waste. The increase on the concentration of the concentration of modifying agent (thioglycolic acid) has elevated the presence of sulfhydryl groups, which rised the adsorption capacity of cassava waste. The optimized adsorptions were achieved in less than 30 min. The order of maximum adsorption capacity among the three heavy metal ions was as follows: Zn^{2+} > Cu^{2+} > Cd^{2+}, and the adsorption capacities of modified cassava waste were reported to be 647.48 mg Cd/g and 559.74 mg Zn/g, comparing to only 86.68 mg Cd/g and 55.82 mg Zn/g when using raw cassava waste.[231,232]

Also trying to find a great adsorbent material from agricultural sources to remove heavy metals from water, Oyewo and co-workes (2016) transformed banana peel in a nanosorbent for the removal of radioactive minerals from real mine water. The functional groups responsible for the banana peels capability to coordinate and remove metal ions (uranium and thorium) were identified at absorption bands of 1730 cm^{-1} (carboxylic groups) and 889 cm^{-1} (amine groups) via FTIR analysis. The authors found a maximum adsorption capacity of 27.1 mg g^{-1}, 34.13 mg g^{-1} for uranium and 45.5 mg g^{-1}, 10.10 mg g^{-1} for thorium in synthetic and real mine water, respectively. These results indicated a prospective adsorbent material for the removal of radioactive substances from aqueous solution and also from real mine water, always observing the target pollutant to apply a more suitable material.[233,234] In a review discussing the conversion of banana waste into adsorbents materials and its applications to remove various types of water-soluble pollutants, it was possible to observe several advantages of use this agrigultural waste. Such features are low cost, widely avaiability, and protecting environment by preventing methane/CO$_2$ gas formation due to unsafe damping in wetlands (aerobic and anaerobic decomposition of banana tree waste can produce methane gas) or burning (CO$_2$). It was possible to obeserve that modifications on the adorbent can improve its surface area and expose some functional groups that can improve the adsorption capacity of different pollutant types. It was also possible to highlight that there is a gap in research of the adsorption mechanism involving banana-derived adsorbents and water pollutants, on the other hand, as expressed on Figure 12, banana tree can provide several parts that can be used as adsorbent and were already tested to remove metals, dyes, pesticides, radionuclides, inorganic anions and a huge variety of organic pollutants. Nevertheless, the authors have concluded that, besides the mechanistic studies, cost studies must be conducted to stimulate the industrial use of nonconventional adsorbents. The use of biomass-derived adsorbents in wastewater industries are strongly recommended owing to cheaper and readily available, user-friendly technology, and environmentally sustainable operations.[234]

Figure 12. Different parts of banana tree applied to remove pollutants from water and wastewater.[234]

Another highly important culture with great potential to be have their wastes transformed into adsorbents are beans. Etorki and co-workers (2014) used Fava Beans as low cost adsorbent material for removal of Pb(II), Cd(II) and Zn(II) ions from aqueous solutions. The authors have investigated the use of the adsorbent to treat real taken from batteries factory. The authors found that the best conditions to remove Pb(II), where pH = 3.0, contact time was 1:30 h and adsorbent concentration was 0.5 g.[235]

As a prominent culture, already known and widespread in several places around the world, the Açaí also had its residues studied and transformed into adsorbent materials. Waste from the açai processing industry, for added value concerns, was used as biomass for energy production, additionaly, the biochar resulting from this process was activated with pure NaOH and applied as adsorbent to remove Methylene Blue and reactive dyes from raw textile effluents. Relevant modifications were observed on the adsorbent surface after its activation. A increase in its specific surface area from 1.94 to 491.90 m^2 g^{-1} have led to an expressive rise in its adsorption capacity for Methylene Blue from 33.73 to 93.23 mg g^{-1}. Activated carbon from açaí was also studied on the adsorption of raw textile wastewater, achieving a reduction of 84.62% in the Biochemical Oxygen Demand, these remarks are a special motivation to research and investiments on the use of agricultural waste for environmental remediation, since the waste here have been used not only to generate energy but to help in real wastewater purification.[235]

Finally, wastes from coconut trees and its applications. As alreary pointed, coconut trees are on top level of importance for several reasons, their large presence in many countries on the world and especially the huge amount of theses trees in the Brazilian coast. Coconut has higly economical impact and social relevance, however their waste is still worth of study and used in many different ways. For instance, Yasdi and co-workers (2021), have pointed out the use of coconut shell-based activated carbon to treat real wastewater from kitchen restaurant by reducing the Biochemical Oxygen Demand (BOD). The authors have activated the adsorbent using acid an base. The results showed that the best activator for coconut shell carbon was H_3PO_4 3 M. The adsorption process's optimum pH was at pH 3 with an adsorption percentage of 88.626% and contact time of 10 minutes.[236]

Additionally, Nandeshwar and co-workers (2016) have used coconut shells carbonized at 500° C and activated with HCl, HNO_3, H_2SO_4 as adsorbent to remove iron from real industrial wastewater samples from villages near Nag River (India). Their results showed a high increase on the adsorption capacity after the activation process by all acids used, probably by the elevation of the surface area from (9–11 cm^2/g) to (HCl, 754 cm^2/g; HNO_3, 542 cm_2/g; H_2SO_4, 511 cm_2/g). The adsorption experiments provided a corrobotation to the effect of activation, in case of activated carbons prepared from coconut shells, the material activated by (HNO_3) gave the highest iron removal for all samples (A, 85%; B, 77%; C, 82%; D, 76%; E, 72%). The respective iron removals for the case the material activated by (HCl) were also high (A, 70%; B, 75%; C, 81%; D, 75%; E, 68%), but when sulfuric acid was used for activation the removals were slightly lower (A, 68%; B, 72%; C, 76%; D, 74%; E, 66%). In comparison with the respective removals for non-activated material, the iron removal was quite low (A, 36%; B, 38%; C, 57%; D, 54%; E, 57%). This pointedly demonstrates the effect of activation on the adsorption capability of the adsorbents prepared materials prepared from agricultural wastes.[237]

With the points highlighted in this topic and in the previous ones, it is possible to understand the valuable possibility of the application of agricultural residues in the treatment of effluents acting as adsorbents. It is undeniable that there is a large gap between the various studies on a laboratory scale and the transfer of the application to real treatment systems. This gap is evidenced by the low number of studies involving treatment of real effluents on bench scale, on pilot scale and the transformation of these materials into commercial product for industrial application. The points shown aim to highlight Brazil with its great agricultural capacity, which in turn generates a large amount of solid waste from these activities. The use of residues in the preparation of adsorbent materials, which can be considered as value-added materials, aims to solve two environmental problems in parallel. The destination of the large amount of solid waste that still does not have proper application and disposal, and the large amount of liquid waste that can be treated using low-cost adsorbents. The production of these adsorbent materials lead to a resolution to the current problem of the adsorption phase in the treatment of effluents, where the highest associated cost is related to the price and quantity of the adsorbent materials used.

6. Concluding Remarks

Currently, it is mandatory to search for economically viable alternatives that aim to reduce energy expenditure and the raw material. In the field of liquid waste, population growth points to exponential industrial growth. This inevitable reality enhances the search for more effective waste treatment methods, to the point of exacerbating reuse, reducing the search for primary sources. In this field, the work described here sought to shed light on the diversity of agricultural crops present in a country of continental dimensions like Brazil, which produces a large amount of food and consequently generates a large amount of solid and liquid waste. In addition, it is worth noting that such agricultural crops of high relevance in Brazil are also found scattered throughout the world. The work showed the economic importance of these crops, highlighting the amount produced and the associated value, as well as incorporating this amount and this importance with environmental issues. The growing interest in the use of natural materials in studies involving effluent treatment via adsorption was shown through a bibliometric analysis. Then, details of how these adsorbent materials can be prepared and directed to greater adsorption efficiency were discussed, when the characteristics of each material and each synthesis variable are known by appropriate techniques for characterizing structures and surfaces. Finally, the gap between laboratory-scale studies and the end of the production chain, which is the commercial and industrial application of these low-cost adsorbent materials from agricultural waste, was highlighted. It was evident that the use of these materials can solve the problem of solid waste that needs to be disposed of properly and liquid waste that needs to be treated so that the water is returned to water bodies and reused.

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References

1. Elhacham, E.; Ben-Uri, L.; Grozovski, J.; Bar-On, Y. M.; Milo, R.; Global human-made mass exceeds all living biomass. *Nature* **2020**, *588*, 442. [Crossref]
2. Oliveira, L. M. T. M.; Oliveira, L. F. A. M.; Sonsin, A. F.; Duarte, J. L. S.; Soletti, J. I.; Fonseca, E. J. S.; Ribeiro, L. M. O.; Meili,

L.; Ultrafast diesel oil spill removal by fibers from silk-cotton tree: characterization and sorption potential evaluation. *Journal of Cleaner Production* **2020,** 263, 121448. [Crossref]

3. Popp, J.; Kovács, S.; Oláh, J.; Divéki, Z.; Balázs, E.; Bioeconomy: biomass and biomass-based energy supply and demand. *New Biotechnology* **2021**, 60, 76. [Crossref] [PubMed]
4. The World Bank. (April, 2022). Agriculture and Food. Available: <https://www.worldbank.org/en/topic/agriculture/overview>. Accessed in: 24th July 2022.
5. EMBRAPA, Empresa Brasileira de Pesquisa Agropecuária, 2020. Available: <https://www.embrapa.br/mandioca-e-fruticultura>. Accessed in: 24th July 2022.
6. EMBRAPA. (2018). Visão 2030: o futuro da agricultura brasileira. Embrapa. Empresa Brasileira de Pesquisa Agropecuária & Júnior, S. V. (2020). Aproveitamento de resíduos agroindustriais: Uma abordagem sustentável. Embrapa Agroenergia. Available: <https://www.embrapa.br/documents/10180/9543845/Vis%C3%A3o+2030+-+o+futuro+da+agricultura+brasileira/2a9a0f27-0ead-991a-8cbf-af8e89d62829?version=1.1>. Accessed in: 24th July 2022.
7. IBGE. (2022, junho). LSPA - Levantamento Sistemático da Produção Agrícola- Área, Produção e Rendimento Médio - Confronto das Safras de 2021 e das Estimativas para 2022 - Brasil. Instituto Brasileiro de Geografia e Estatística. Retrieved Júlio 15, 2022, from <https://www.ibge.gov.br/estatisticas/economicas/agricultura-e-pecuaria/9201-levantamento-sistematico-da-producao-agricola.html?=&t=resultados> Accessed in: 24th July 2022.
8. FAO, Food and Agricultural Organization of the United Nations. Agricultural production statistics 2000–2020. <https://www.fao.org/3/cb9180en/cb9180en.pdf>. Accessed in: 24th July 2022.
9. dos Santos, L. J. C. M.; Azevedo, G. N.; Uso de adsorventes como alternativa no tratamento de contaminantes orgânicos em águas e efluentes líquidos. *Boletim do Observatório Ambiental Alberto Ribeiro Lamego* **2019**, *13*, 68. [Crossref]
10. Lermen, A. M.; Fronza, C. S.; Diel, J. C.; Schein, D.; Clerici, N. J.; Guimarães, R. E.; Boligon, S. D.; Scher, A. C.; A utilização de resíduos agroindustriais para adsorção do corante azul de metileno: uma breve revisão / The use of agro-industrial waste for adsorption of the blue dye of methylene: a brief review. *Brazilian Applied Science Review* **2021**, *5*, 273. [Crossref]
11. Antunes, E. C. E. S.; Pereira, J. E. S.; Ferreira, R. L. S.; Medeiros, M. F. D.; Neto, E. L. B.; Remoção de corante têxtil utilizando a casca do abacaxi como adsorvente natural. *HOLOS* **2018**, *3*, 81. [Crossref]
12. Santos, D. H. S.; Paulino, J. C. P. L.; Alves, G. F. S.; Oliveira, L. M. T. M.; Nagliate, P. C.; Duarte, J. L. S.; Meili, L.; Tonholo, J.; Zanta, C. L. P. S.; Effluent treatment using activated carbon adsorbents: a bibliometric analysis of recent literature. *Environmental Science and Pollution Research* **2021**, *28*, 32224. [Crossref]
13. Ahmad, A.; Mohd-Setapar, S. H.; Chuong, C. S.; Khatoon, A.; Wani, W. A.; Kumar, R.; Rafatullah, M.; Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater. *RSC Advances* **2015**, *5*, 30801. [Crossref].
14. Frantz, T. S.; *Tese de Doutorado*, Universidade Federal do Rio Grande, 2020. [Link]
15. Bazargan, A.; Tan, J.; McKay, G.; Standardization of oil sorbent performance testing. *Journal of Testing and Evaluation* **2015**, *43*, 1271. [Crossref].
16. Santos-Pereira, G. C.; Corso, C. R.; Forss, J.; Evaluation of two different carriers in the biodegradation process of an azo dye. *Journal of Environmental Health Science & Engineering* **2019**, *17*, 633. [Crossref] [PubMed]
17. Nasra, E.; Kurniawati, D.; Etika, S. B.; Silvia, R.; Rahmatika, A.; Effect of pH and concentration on biosorption malachite green and rhodamine b dyes using banana peel (*Musa balbisiana* Colla) as biosorbent. *Journal of Physics: Conference Series* **2021**, *1788*, 012003. [Crossref]
18. Oliveira, L. M. T. M.; Saleem, J.; Bazargan, A.; Duarte, J. L. da S.; McKay, G.; Meili, L.; Sorption as a rapidly response for oil spill accidents: A material and mechanistic approach. *Journal of Hazardous Materials* **2021**, *407*, 124842. [Crossref] [PubMed]
19. Karimi-Maleh, H.; Ayati, A.; Davoodi, R.; Tanhaei, B.; Karimi, F.; Malekmohammadi, S.; Orooji, Y.; Fu, L.; Sillanpää, M.; Recent advances in using of chitosan-based adsorbents for removal of pharmaceutical contaminants: A review. *Journal of Cleaner Prodution* **2021**, *291*, 125880. [Crossref]
20. Kajeiou, M.; Alem, A.; Mezghich, S.; Ahfir, N. D.; Mignot, M.; Devouge-Boyer, C.; Pantet, A.; Competitive and non-competitive zinc, copper and lead biosorption from aqueous solutions onto flax fibers. *Chemosphere* **2020**, *260*, 127505. [Crossref] [PubMed]
21. Quintela, D. U.; Henrique, D. C.; dos Santos Lins, P. V.; Ide, A. H.; Erto, A.; Duarte, J. L. da S.; Meili, L.; Waste of *Mytella falcata* shells for removal of a triarylmethane biocide from water: Kinetic, equilibrium, regeneration and thermodynamic studies. *Colloids Surfaces B Biointerfaces* **2020**, *195*, 111230. [Crossref] [PubMed]
22. Bhargava, D. S.; Sheldarkar, S. B.; Use of TNSAC in phosphate adsorption studies and relationships. Literature, experimental methodology, justification and effects of process variables. *Water Research* **1993**, *27*, 303. [Crossref]
23. Bhargava, D. S.; Sheldarkar, S. B.; Use of TNSAC in phosphate adsorption studies and relationships. Effects of adsorption operating variables and related relationships. *Water Research* **1993**, *27*, 313. [Crossref]
24. Bhargava, D. S.; Sheldarkar, S. B.; Use of TNSAC in phosphate adsorption studies and relationships. Isotherm relationships and utility in the field. *Water Research* **1993**, *27*, 325. [Crossref]
25. Periasamy, K.; Namasivayam, C.; Process development for removal and recovery of cadmium from wastewater by a low-cost adsorbent: adsorption rates and equilibrium studies. *Industrial & Engineering Chemistry Research* **1994**, *33*, 317. [Crossref]
26. Namasivayam, C.; Kadirvelu, K.; Coirpith, an agricultural waste by-product, for the treatment of dyeing wastewater. *Bioresource Technology* **1994**, *48*, 79. [Crossref]
27. Vázquez, G.; Antorrena, G.; González, J.; Doval, M. D.; Adsorption of heavy metal ions by chemically modified *Pinus pinaster* bark. *Bioresource Technology.* **1994**, *48*, 251. [Crossref]
28. Marshall, W. E.; Champagne, E. T.; Agricultural byproducts as

adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. *Journal of Environmental Science and Health, Part A,* **2008**, *30*, 241. [Crossref]

29. El-Geundi, M. S.; Adsorbents for industrial pollution control. *Adsorption Science and Technology* **2016**, *15*, 777. [Crossref]
30. Mohan, D.; Singh, K. P.; Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste. *Water Research* **2002**, *36*, 2304. [Crossref] [PubMed]
31. Babel, S.; Kurniawan, T. A.; Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* **2004**, *54*, 951. [Crossref] [PubMed]
32. Crini, G.; Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology* **2006**, *97*, 1061. [Crossref] [PubMed]
33. Gupta, V. K.; Application of low-cost adsorbents for dye removal – A review. *Journal of Environmental Management* **2009**, *90*, 2313. [Crossref] [PubMed]
34. Miretzky, P.; Cirelli, A. F.; Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review. *Journal of Hazardous Materials* **2010**, *180*, 1. [Crossref] [PubMed]
35. Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A.; Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials* **2010**, *177*, 70. [Crossref] [PubMed]
36. Adegoke, K. A.; Bello, O. S.; Dye sequestration using agricultural wastes as adsorbents. *Water Resource and Industry* **2015**, *12*, 8. [Crossref]
37. Bhatnagar, A.; Sillanpää, M.; Witek-Krowiak, A.; Agricultural waste peels as versatile biomass for water purification – A review. *Chemical Engineering Journal* **2015**, *270*, 244. [Crossref]
38. Ali, R. M.; Hamad, H. A.; Hussein, M. M.; Malash, G. F.; Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecological Engineering* **2016**, *91*, 317. [Crossref]
39. Thines, K. R.; Abdullah, E. C.; Mubarak, N. M.; Ruthiraan, M.; Synthesis of magnetic biochar from agricultural waste biomass to enhancing route for waste water and polymer application: a review. *Renewable and Sustainable Energy Reviews* **2017**, *67*, 257. [Crossref]
40. Afroze, S.; Sen, T. K. A.; Review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water, Air, & Soil Pollution* **2018**, *229*, 1. [Crossref]
41. Burakov, A. E.; Galunin, E. V.; Burakova, I. V.; Kucherova, A. E.; Agarwal, S.; Tkachev, A. G.; Gupta, V. K.; Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review. *Ecotoxicology and Environmental Safety* **2018**, *148*, 702. [Crossref] [PubMed]
42. Joseph, L.; Jun, B. M.; Flora, J. R. V.; Park, C. M.; Yoon, Y.; Removal of heavy metals from water sources in the developing world using low-cost materials: a review. *Chemosphere* **2019**, *229*, 142. [Crossref] [PubMed]
43. Abuelnoor, N.; AlHajaj, A.; Khaleel, M.; Vega, L. F.; Abu-Zahra, M. R. M.; Activated carbons from biomass-based sources for CO_2 capture applications. *Chemosphere* **2021**, *282*, 131111. [Crossref] [PubMed]
44. Aryee, A. A.; Mpatani, F. M.; Kani, A. N.; Dovi, E.; Han, R.; Li, Z.; Qu, L.; A review on functionalized adsorbents based on peanut husk for the sequestration of pollutants in wastewater: modification methods and adsorption study. *Journal of Cleaner Production* **2021**, *310*, 127502. [Crossref]
45. Liu, Z.; Wang, Z.; Chen, H.; Cai, T.; Liu, Z.; Hydrochar and pyrochar for sorption of pollutants in wastewater and exhaust gas: a critical review. *Environmental Pollution* **2021**, *268*, 115910. [Crossref] [PubMed]
46. Dawn, S.; Vishwakarma, V.; Recovery and recycle of wastewater contaminated with heavy metals using adsorbents incorporated from waste resources and nanomaterials - a review. *Chemosphere* **2021**, *273*, 129677. [Crossref] [PubMed]
47. Xue, H.; Wang, X.; Xu, Q.; Dhaouadi, F.; Sellaoui, L.; Seliem, M. K.; Ben Lamine, A.; Belmabrouk, H.; Bajahzar, A.; Bonilla-Petriciolet, A.; Li, Z.; Li, Q.; Adsorption of methylene blue from aqueous solution on activated carbons and composite prepared from an agricultural waste biomass: a comparative study by experimental and advanced modeling analysis. *Chemical Engineering Journal* **2022**, *430*, 132801. [PubMed]
48. Venceslau, A. de F. A.; Mendonça, A. C.; Carvalho, L. B.; Ferreira, G. M. D.; Thomasi, S. S.; Pinto, L. M. A.; Removal of methylene blue from an aqueous medium using atemoya peel as a low-cost adsorbent. *Water, Air, & Soil Pollution* **2021**, *232*, 1. [Crossref]
49. Januário, E. F. D.; Vidovix, T. B.; Araújo, L. A. de; Bergamasco Beltran, L.; Bergamasco, R.; Vieira, A. M. S.; Investigation of *Citrus reticulata* peels as an efficient and low-cost adsorbent for the removal of safranin orange dye. *Environmental Technology* **2022**, *43*, 4315. [Crossref] [PubMed]
50. Da, A.; Schiller, P.; Gonçalves, C.; De Lucca Braccini, A.; Schwantes, D.; Campagnolo, M. A.; Conradi, E.; Zimmermann, J.; Potential of agricultural and agroindustrial wastes as adsorbent materials of toxic heavy metals: a review. *Desalination and Water Treatment* **2020**, 187, 203. [Crossref]
51. Anastopoulos, I.; Pashalidis, I.; Hosseini-Bandegharaei, A.; Giannakoudakis, D. A.; Robalds, A.; Usman, M.; Escudero, L. B.; Zhou, Y.; Colmenares, J. C.; Núñez-Delgado, A.; Lima, É. C.; Agricultural biomass/waste as adsorbents for toxic metal decontamination of aqueous solutions. *Journal of Molecular Liquids* **2019**, *295*, 111684. [Crossref]
52. Sajjadi, S. A.; Mohammadzadeh, A.; Tran, H. N.; Anastopoulos, I.; Dotto, G. L.; Lopičić, Z. R.; Sivamani, S.; Rahmani-Sani, A.; Ivanets, A.; Hosseini-Bandegharaei, A.; Efficient mercury removal from wastewater by pistachio wood wastes-derived activated carbon prepared by chemical activation using a novel activating agent. *Journal of Environmental Management* **2018**, *223*, 1001. [Crossref] [PubMed]
53. Gao, B.; Chang, Q.; Yang, H.; Selective adsorption of ofloxacin and ciprofloxacin from a binary system using lignin-based adsorbents: Quantitative analysis, adsorption mechanisms, and structure-activity relationship. *Science of the Total Environment* **2021**, *765*, 144427. [Crossref] [PubMed]

54. Djilani, C.; Zaghdoudi, R.; Djazi, F.; Bouchekima, B.; Lallam, A.; Modarressi, A.; Rogalski, M.; Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon. *Journal of the Taiwan Institute of Chemical Engineers* **2015**, *53*, 112. [Crossref]
55. Arris, S.; Bencheikh, L. M.; Miniai, H. A.; Preparation and characterisation of an natural adsorbent used for elimination of pollutants in wastewater. *Energy Procedia* **2012**, *18*, 1145. [Crossref]
56. Kaur, B.; Kalra, P.; Kaur, N.; *Prosopis juliflora* (Kikar) pods as adsorbent for removal of Cd(II) ions from aqueous streams. *Materials Today: Proceedings* **2022**, *68*, 809. [Crossref]
57. Solangi, N. H.; Kumar, J.; Mazari, S. A.; Ahmed, S.; Fatima, N.; Mubarak, N. M.; Development of fruit waste derived bio-adsorbents for wastewater treatment: a review. *Journal of Hazardous Materials* **2021**, *416*, 125848. [Crossref]
58. Varbanov, P. S.; Walmsley, T. G.; Klemeš, J. J.; Seferlis, P.; Van Fan, Y.; Klemeš, J. J.; Tan, R. R.; Varbanov, S.; Graphical Break-Even Based Decision-Making Tool (BBDM) to Minimise GHG Footprint of Biomass Utilisation: Biochar by Pyrolysis. *Chemical Engineering Transactions* **2019**, *76*, 19. [Crossref]
59. Czajczyńska, D.; Anguilano, L.; Ghazal, H.; Krzyżyńska, R.; Reynolds, A. J.; Spencer, N.; Jouhara, H.; Potential of pyrolysis processes in the waste management sector. *Thermal Science and Engineering Progress* **2017**, *3*, 171. [Crossref]
60. Neves, D.; Thunman, H.; Matos, A.; Tarelho, L.; Gómez-Barea, A.; Characterization and prediction of biomass pyrolysis products. *Progress in Energy and Combustion Science* **2011**, *37*, 611. [Crossref]
61. Pariyar, P.; Kumari, K.; Jain, M. K.; Jadhao, P. S.; Evaluation of change in biochar properties derived from different feedstock and pyrolysis temperature for environmental and agricultural application. *Science of the Total Environment* **2020**, *713*, 136433. [Crossref] [PubMed]
62. Usino, D. O.; Supriyanto; Ylitervo, P.; Pettersson, A.; Richards, T.; Influence of temperature and time on initial pyrolysis of cellulose and xylan. *Journal of Analytical and Applied Pyrolysis* **2020**, *147*, 104782. [Crossref]
63. Ateş, F.; Işikdağ, M. A.; Evaluation of the role of the pyrolysis temperature in straw biomass samples and characterization of the oils by GC/MS. *Energy and Fuels* **2008**, *22*, 1936. [Crossref]
64. Pecha, M. B.; Montoya, J. I.; Ivory, C.; Chejne, F.; Garcia-Perez, M.; modified pyroprobe captive sample reactor: characterization of reactor and cellulose pyrolysis at vacuum and atmospheric pressures. *Industrial & Engineering Chemistry Research* **2017**, *56*, 5185. [Crossref]
65. Demirbas, A.; Effect of Temperature on Pyrolysis Products from Biomass. *Energy Sources Part A: Recovery, Utilization, and Environmental Effects*. **2010**, *29*, 329. [Crossref]
66. Ojha, D. K.; Viju, D.; Vinu, R.; Fast pyrolysis kinetics of alkali lignin: Evaluation of apparent rate parameters and product time evolution. *Bioresource Technology* **2017**, *241*, 142. [Crossref] [PubMed]
67. Zhang, Y.; Zheng, R.; Zhao, J.; Ma, F.; Zhang, Y.; Meng, Q.; Characterization of H_3PO_4-treated rice husk adsorbent and adsorption of Copper(II) from aqueous solution. *BioMed Research International* **2014**, *2014*, [CrossRef] [PubMed]
68. Amen, R.; Yaseen, M.; Mukhtar, A.; Klemeš, J. J.; Saqib, S.; Ullah, S.; Al-Sehemi, A. G.; Rafiq, S.; Babar, M.; Fatt, C. L.; Ibrahim, M.; Asif, S.; Qureshi, K. S.; Akbar, M. M.; Bokhari, A.; Lead and cadmium removal from wastewater using eco-friendly biochar adsorbent derived from rice husk, wheat straw, and corncob. *Cleaner Engineering and Technology* **2020**, *1*, 100006. [Crossref]
69. Steigerwald, J. M.; Ray, J. R.; Adsorption behavior of perfluorooctanesulfonate (PFOS) onto activated spent coffee grounds biochar in synthetic wastewater effluent. *Journal of Hazardous Materials Letters* **2021**, *2*, 100025. [Crossref]
70. Liu, N.; Charrua, A. B.; Weng, C. H.; Yuan, X.; Ding, F.; Characterization of biochars derived from agriculture wastes and their adsorptive removal of atrazine from aqueous solution: a comparative study. *Bioresource Technology* **2015**, *198*, 55. [Crossref] [PubMed]
71. Manyatshe, A.; Cele, Z. E. D.; Balogun, M. O.; Nkambule, T. T. I.; Msagati, T. A. M.; Chitosan modified sugarcane bagasse biochar for the adsorption of inorganic phosphate ions from aqueous solution. *Journal of Environmental Chemical Engineering* **2022**, *10*, 108243. [Crossref]
72. Zhang, S.; Abdalla, M. A. S.; Luo, Z.; Xia, S.; The wheat straw biochar research on the adsorption/desorption behaviour of mercury in wastewater. *Desalination and Water Treatment* **2017**, 112, 147. [Crossref]
73. Sun, J.; Lian, F.; Liu, Z.; Zhu, L.; Song, Z.; Biochars derived from various crop straws: characterization and Cd(II) removal potential. *Ecotoxicology and Environmental Safety* **2014**, *106*, 226. [Crossref] [PubMed]
74. Jian, X.; Zhuang, X.; Li, B.; Xu, X.; Wei, Z.; Song, Y.; Jiang, E.; Comparison of characterization and adsorption of biochars produced from hydrothermal carbonization and pyrolysis. *Environmental Technology & Innovation* **2018**, *10*, 27. [Crossref]
75. Wu, J.; Yang, J.; Huang, G.; Xu, C.; Lin, B.; Hydrothermal carbonization synthesis of cassava slag biochar with excellent adsorption performance for Rhodamine B. *Journal of Cleaner Production* **2020**, *251*, 119717. [Crossref]
76. Román, S.; Ledesma, B.; Álvarez-Murillo, A.; Sabio, E.; González, J. F.; González, C. M.; Production of cost-effective mesoporous materials from prawn shell hydrocarbonization. *Nanoscale Research Letters* **2016**, *11*, 1. [Crossref]
77. Liu, F.; Yu, R.; Ji, X.; Guo, M.; Hydrothermal carbonization of holocellulose into hydrochar: Structural, chemical characteristics, and combustion behavior. *Bioresource Technology* **2018**, *263*, 508. [Crossref] [PubMed].
78. Busch, D.; Stark, A.; Kammann, C. I.; Glaser, B.; Genotoxic and phytotoxic risk assessment of fresh and treated hydrochar from hydrothermal carbonization compared to biochar from pyrolysis. *Ecotoxicology and Environmental Safety* **2013**, *97*, 59. [Crossref] [PubMed]
79. Shaheen, S. M.; Niazi, N. K.; Hassan, N. E. E.; Bibi, I.; Wang, H.; Tsang, D. C. W.; Ok, Y. S.; Bolan, N.; Rinklebe, J.; Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review. *International Materials Reviews* **2018**, *64*, 216. [Crossref]

80. Nizamuddin, S.; Baloch, H. A.; Griffin, G. J.; Mubarak, N. M.; Bhutto, A. W.; Abro, R.; Mazari, S. A.; Ali, B. S.; An overview of effect of process parameters on hydrothermal carbonization of biomass. *Renewable and Sustainable Energy Reviews* **2017**, *73*, 1289. [Crossref]
81. Zhang, X.; Li, Y.; Wang, M.; Han, L.; Liu, X.; Effects of Hydrothermal Carbonization Conditions on the Combustion and Kinetics of Wheat Straw Hydrochar Pellets and Efficiency Improvement Analyses. *Energy & Fuels* **2019**, *34*, 587. [Crossref]
82. Danso-Boateng, E.; Mohammed, A. S.; Sander, G.; Wheatley, A. D.; Nyktari, E.; Usen, I. C.; Production and characterisation of adsorbents synthesised by hydrothermal carbonisation of biomass wastes. *SN Applied Sciences* **2021**, *3*, 1. [Crossref]
83. Thawornchaisit, U.; Onlamai, T.; Phurkphong, N.; Sukharom, R.; Sugarcane bagasse-derived hydrochar: modification with cations to enhance phosphate removal. *Environment and Natural Resources Journal* **2021**, *19*, 371. [Crossref]
84. Liu, C.; Wang, W.; Wu, R.; Liu, Y.; Lin, X.; Kan, H.; Zheng, Y.; Preparation of acid- and alkali-modified biochar for removal of methylene blue pigment. *ACS Omega* **2020**, *5*, 30906. [Crossref].
85. Canales-Flores, R. A.; Prieto-García, F.; activation methods of carbonaceous materials obtained from agricultural waste. *Chemistry & Biodiversity* **2016**, *13*, 261. [Crossref]
86. Ukanwa, K. S.; Patchigolla, K.; Sakrabani, R.; Anthony, E.; Mandavgane, S.; A review of chemicals to produce activated carbon from agricultural waste biomass. *Sustainability* **2019**, *11*, 6204. [Crossref]
87. Piriya, R. S.; Jayabalakrishnan, R. M.; Maheswari, M.; Coconut shell-based activated carbon for wastewater treatment. *Abstracts of International Conferences & Meetings* **2021**, 1, 18. [Crossref]
88. Fathy, N. A.; El-Shafey, O. I.; Khalil, L. B.; Effectiveness of alkali-acid treatment in enhancement the adsorption capacity for rice straw: the removal of methylene blue dye. *ISRN Physical Chemistry.* **2013**, 15,1. [Crossref]
89. Mariana, M.; Mulana, F.; Juniar, L.; Fathira, D.; Safitri, R.; Muchtar, S.; Bilad, M. R.; Shariff, A. H. M.; Huda, N.; Development of biosorbent derived from the endocarp waste of gayo coffee for lead removal in liquid wastewater—effects of chemical activators. *Sustainability* **2021**, 13, 3050. [Crossref]
90. Da Penha Bezerra, W. F.; Dognani, G.; De Alencar, L. N.; Parizi, M. P. S.; Boina, R. F.; Cabrera, F. C.; Job, A. E.; Chemical treatment of sugarcane bagasse and its influence on glyphosate adsorption. *Matéria* (Rio Janeiro) **2022**, 27, [Crossref]
91. Tang, Y.; Li, Y.; Zhan, L.; Wu, D.; Zhang, S.; Pang, R.; Xie, B.; Removal of emerging contaminants (bisphenol A and antibiotics) from kitchen wastewater by alkali-modified biochar. *Science of the Total Environment* **2022**, *805*, 150158. [Crossref]
92. Nam, H.; Choi, W.; Genuino, D. A.; Capareda, S. C.; Development of rice straw activated carbon and its utilizations. *Journal of Environmental Chemical Engineering* **2018**, *6*, 5221. [Crossref]
93. Tee, G. T.; Gok, X. Y.; Yong, W. F.; Adsorption of pollutants in wastewater via biosorbents, nanoparticles and magnetic biosorbents: a review. *Environmental Research* **2022**, *212*, 113248. [Crossref]
94. Knapczyk, A.; Francik, S.; Jewiarz, M.; Zawiślak, A.; Francik, R.; Thermal treatment of biomass: a bibliometric analysis—the torrefaction case. *Energies* ***2021,*** 14, 162. [Crossref]
95. Boakye, P.; Ohemeng-Boahen, G.; Darkwah, L.; Sokama-Neuyam, Y. A.; Appiah-Effah, E.; Oduro-Kwarteng, S.; Asamoah Osei, B.; Asilevi, P. J.; Woo, S. H.; Waste biomass and biomaterials adsorbents for wastewater treatment. *Green Energy and Environmental Technology* **2022**, *2022*, 1. [Crossref]
96. Sajjadi, B.; Chen, W. Y.; Mattern, D. L.; Hammer, N.; Dorris, A.; Low-temperature acoustic-based activation of biochar for enhanced removal of heavy metals. *Journal of Water Process Engineering* **2020**, *34*, 101166. [Crossref]
97. Karami, S.; Papari, S.; Berruti, F.; Conversion of waste corn biomass to activated bio-char for applications in wastewater treatment. *Frontiers in Materials* **2022**, *9*, 226. [Crossref]
98. Lee, K. T.; Cheng, C. L.; Lee, D. S.; Chen, W. H.; Vo, D. V. N.; Ding, L.; Lam, S. S.; Spent coffee grounds biochar from torrefaction as a potential adsorbent for spilled diesel oil recovery and as an alternative fuel. *Energy* **2022**, *239*, 122467. [Crossref]
99. Vieira, A. M. S.; Vieira, M. F.; Silva, G. F.; Araújo, Á. A.; Fagundes-Klen, M. R.; Veit, M. T.; Bergamasco, R.; Use of *Moringa oleifera* seed as a natural adsorbent for wastewater treatment. *Water, Air, & Soil Pollution* **2010**, *206*, 273. [Crossref]
100. Basak, A.; Rahman Idris, M.; Arifuzzaman, M.; Saha, T.; Yasmin, J.; Cost effective wastewater treatment by natural adsorbent. *Journal of Chemistry and Chemical Sciences* **2018**, *8*, 777. [Crossref]
101. Kahraman, S.; Dogan, N.; Erdemoglu, S.; Use of various agricultural wastes for the removal of heavy metal ions. *International Journal of Environment and Pollution* **2008**, *34*, 275. [Crossref]
102. Rigueto, C. V. T.; Harala, S. C.; Rosseto, M.; Ostwald, B. E. P.; Massuda, L. Á.; Nazari, M. T.; Dettmer, A.; Loss, R. A.; Geraldi, C. A. Q.; Soybean hull as an alternative biosorbent to uptake a reactive textile dye from aqueous solutions. *Matéria (Rio Janeiro)* **2021**, *26*, [Crossref]
103. Alessandretti, I.; Jesus, R. R. de; Guedes, S. F.; Loss, R. A.; Paula, J. M. de; Geraldi, C. A. Q.; Biosorption of direct scarlet red dye by cassava bagasse. *Research, Society and Development* **2021**, *10*, 16510413964. [Crossref]
104. Siqueira, T. C. A.; da Silva, I. Z.; Rubio, A. J.; Bergamasco, R.; Gasparotto, F.; Paccola, E. A. de S.; Yamaguchi, N. U.; Sugarcane bagasse as an efficient biosorbent for methylene blue removal: kinetics, isotherms and thermodynamics. *International Journal of Environmental Research and Public Health* **2020**, *17*, 526. [Crossref]
105. Singh, S.; Kumar, V.; Datta, S.; Dhanjal, D. S.; Sharma, K.; Samuel, J.; Singh, J.; Current advancement and future prospect of biosorbents for bioremediation. *Science of The Total Environment* **2020**, *709*, 135895. [Crossref]
106. Bansal, M.; Mudhoo, A.; Garg, V. K.; Singh, D.; Preparation and characterization of biosorbents and copper sequestration from simulated wastewater. *International Journal of Environmental Science and Technology* **2014**, *11*, 1399. [Crossref]
107. Bavaresco, A.; Fonseca, J. M.; Scheufele, F. B.; da Silva, C.; Teleken, J. G.; Use of carbonized corn cob biomass to reduce

acidity of residual frying oil. *Acta Scientiarum. Technology* **2021**, *43*, e51303. [Crossref]

108. Golveia, J. C. S.; Santiago, M. F.; Silva, L. B.; Campos, L. C.; Schimidt, F.; Utilization of the corncob agro-industrial residue as a potential adsorbent in the biosorption of bisphenol-a. *Journal of the Brazilian Chemical Society* **2021**, *32*, 1396. [Crossref]
109. Jawad, A. H.; Bardhan, M.; Islam, M. A.; Islam, M. A.; Syed-Hassan, S. S. A.; Surip, S. N.; ALOthman, Z. A.; Khan, M. R.; Insights into the modeling, characterization and adsorption performance of mesoporous activated carbon from corn cob residue via microwave-assisted H_3PO_4 activation. *Surfaces and Interfaces* **2020**, *21*, 100688. [Crossref]
110. Frollini, E.; Bartolucci, N.; Sisti, L.; Celli, A.; Poly(butylene succinate) reinforced with different lignocellulosic fibers. *Industrial Crops and Products* **2013**, *45*, 160. [Crossref]
111. Chen, Y.; Chen, Q.; Zhao, H.; Dang, J.; Jin, R.; Zhao, W.; Li, Y.; Wheat straws and corn straws as adsorbents for the removal of Cr(VI) and Cr(III) from aqueous solution: kinetics, isotherm, and mechanism. *ACS Omega* **2020**, *5*, 6003. [Crossref]
112. Furlan, F. L.; Consolin Filho, N.; Consolin, M. F. B.; Gonçalves, M. S.; Valderrama, P.; Genena, A. K.; Use of agricultural and agroindustrial residues as alternative adsorbents of manganese and iron in aqueous solution. *Revista Ambiente & Água* **2018**, *13*, 1. [Crossref]
113. Balomajumder, C.; Chand, S.; A potential of biosorbent derived from banana peel for removal of As (III) from contaminated water. *International Journal of Chemical Sciences and Applications* **2012**, 3, 269. [Link]
114. Marwan, M.; Mulana, F.; Yunardi, Y.; Ismail, T. A.; Hafdiansyah, M. F.; Activation and characterization of waste coffee grounds as bio-sorbent. *IOP Conference Series: Materials Science and Engineering* **2018**, *334*, 012029. [Crossref]
115. Guo, Y.; Zhu, W.; Li, G.; Wang, X.; Zhu, L.; Effect of alkali treatment of wheat straw on adsorption of Cu(II) under acidic condition. *Harmful Chemicals in the Environment* **2016**, *2016*, 6326372. [Crossref]
116. Sousa, A. A. O.; Oliveira, T. S.; Azevedo, L. E. C.; Nobre, J. R. C.; Stefanelli, W. F. R.; Costa, T. A. P. S.; Silva, J. P. S.; Barral, A. V. S.; Adsorption of the basic Malachite Green dye via activated carbon from the açaí seed. *Research, Society and Development* **2021**, *10*, e49110212871. [Crossref]
117. Anirudhan, T. S.; Unnithan, M. R.; Arsenic (V) removal from aqueous solutions using an anion exchanger derived from coconut coir pith and its recovery. *Chemosphere* **2007**, *66*, 60. [Crossref]
118. Ajala, E. O.; Ayanshola, A. M.; Obodo, C. I.; Ajala, M. A.; Ajala, O. J.; Simultaneous removal of Zn(II) ions and pathogens from pharmaceutical wastewater using modified sugarcane bagasse as biosorbents. *Results in Engineering* **2022**, *15*, 100493. [Crossref]
119. Harripersadth, C.; Musonge, P.; Makarfi Isa, Y.; Morales, M. G.; Sayago, A.; The application of eggshells and sugarcane bagasse as potential biomaterials in the removal of heavy metals from aqueous solutions. *South African Journal of Chemical Engineering* **2020**, *34*, 142. [Crossref]
120. Jawad, A. H.; Rashid, R. A.; Azlan, M.; Ishak, M.; Ismail, K.; Adsorptive removal of methylene blue by chemically treated cellulosic waste banana (*Musa sapientum*) peels. *Journal of Taibah University for Science* **2018**, *12*, 809. [Crossref]
121. Palapa, N. R.; Taher, T.; Juleanti, N.; Normah; Lesbani, A.; Biochar from rice husk as efficient biosorbent for procion red removal from aqueous systems. *Applied Environmental Research* **2021**, *43*, 79. [Crossref]
122. Vieira, M. G. A.; De Almeida Neto, A. F.; Carlos Da Silva, M. G.; Nóbrega, C. C.; Melo Filho, A. A.; Characterization and use of in natura and calcined rice husks for biosorption of heavy metals ions from aqueous effluents. *Brazilian Journal of Chemical Engineering.* **2012**, *29*, 619. [Crossref]
123. Awokoya, K. N.; Owoade, O. J.; Moronkola, B. A.; Oguntade, B. K.; Ibikunle, A. A. ; Atewolara-Odule, O. C.; Ogundare, S. A.; Morphological characteristics of cassava peel and its effect on the adsorption of heavy metal ions from aqueous media. *Journal of Multidisciplinary Engineering Science and Technology* **2016**, *3*, 2458. [Link]
124. Verma, R.; Maji, P. K.; Sarkar, S.; Comprehensive investigation of the mechanism for Cr(VI) removal from contaminated water using coconut husk as a biosorbent. *Journal of Cleaner Production* **2021**, *314*, 128117. [Crossref]
125. Tummino, M. L.; Tolardo, V.; Malandrino, M.; Sadraei, R.; Magnacca, G.; Laurenti, E.; A way to close the loop: physicochemical and adsorbing properties of soybean hulls recovered after soybean peroxidase extraction. *Frontiers in Chemistry* **2020**, *8*, [Crossref]
126. Ying, Z.; Chen, X.; Li, H.; Liu, X.; Zhang, C.; Zhang, J.; Yi, G.; Efficient adsorption of methylene blue by porous biochar derived from soybean dreg using a one-pot synthesis method. *Molecules* **2021**, *26*, 661. [Crossref]
127. Peñafiel, M. E.; Matesanz, J. M.; Vanegas, E.; Bermejo, D.; Ormad, M. P.; Corncobs as a potentially low-cost biosorbent for sulfamethoxazole removal from aqueous solution. *Separation Science and Technology* **2019**, *55*, 3060. [Crossref]
128. Assirey, E. A.; Altamimi, L. R.; Chemical analysis of corn cob-based biochar and its role as water decontaminants. *Journal of Taibah University for Science* **2021**, *15*, 111. [Crossref]
129. Meshram, S.; Katiyar, D.; Asha, T.; Dewangan, G. P.; Joshi, A. N.; Thakur, R. S.; Preparation and characterization of activated carbon from spent coffee grounds using NaOH and KCl as activating agents. *Journal of the Indian Chemical Society* **2020**, *97*, 1115. [Link]
130. Quyen, V. thi; Pham, T. H.; Kim, J.; Thanh, D. M.; Thang, P. Q.; Van Le, Q.; Jung, S. H.; Kim, T. Y.; Biosorbent derived from coffee husk for efficient removal of toxic heavy metals from wastewater. *Chemosphere* **2021**, *284*, 131312. [Crossref] [PubMed].
131. Saeed, A. A. H.; Harun, N. Y.; Sufian, S.; Afolabi, H. K.; Al-Qadami, E. H. H.; Roslan, F. A. S.; Rahim, S. A.; Ghaleb, A. A. S.; Production and characterization of rice husk biochar and kenaf biochar for value-added biochar replacement for potential materials adsorption. *Ecological Engineering & Environmental Technology* **2021**, *22*, 1. [Crossref].
132. Tovar, C. T.; Delgado, A. D. G.; Ortiz, A. V.; Characterization of residual biomasses and its application for the removal of lead ions from aqueous solution. *Applied Sciences* **2019**, *9*, 4486. [Crossref].

133. Prapagdee, S.; Piyatiratitivorakul, S.; Petsom, A.; Activation of cassava stem biochar by physico-chemical method for stimulating cadmium removal efficiency from aqueous solution. *EnvironmentAsia* **2014**, *7*, 60. [Crossref]
134. Srivastava, S.; Agrawal, S. B.; Mondal, M. K.; Characterization, isotherm and kinetic study of Phaseolus vulgaris husk as an innovative adsorbent for Cr(VI) removal. *Korean Journal of Chemical Engineering* **2015**, *33*, 567. [Crossref]
135. Pradhan, S.; Abdelaal, A. H.; Mroue, K.; Al-Ansari, T.; Mackey, H. R.; McKay, G.; Biochar from vegetable wastes: agro-environmental characterization. *Biochar* **2020**, *2*, 439. [Crossref]
136. Tan, X.; Gao, B.; Xu, X.; Wang, Y.; Ling, J.; Yue, Q.; Li, Q.; Perchlorate uptake by wheat straw based adsorbent from aqueous solution and its subsequent biological regeneration. *Chemical Engineering Journal* **2012**, *211–212*, 37. [Crossref]
137. Kumar, A.; Bhattacharya, T.; Shaikh, W. A.; Roy, A.; Mukherjee, S.; Kumar, M.; Performance evaluation of crop residue and kitchen waste-derived biochar for eco-efficient removal of arsenic from soils of the Indo-Gangetic plain: a step towards sustainable pollution management. *Environmental Research* **2021**, *200*, 111758. [Crossref]
138. Dey, S.; Haripavan, N.; Basha, S. R.; Babu, G. V.; Removal of ammonia and nitrates from contaminated water by using solid waste bio-adsorbents. *Current Research in Chemical Biology* **2021**, *1*, 100005. [Crossref]
139. Su, L.; Chen, M.; Zhuo, G.; Ji, R.; Wang, S.; Zhang, L.; Zhang, M.; Li, H.; Comparison of biochar materials derived from coconut husks and various types of livestock manure, and their potential for use in removal of H_2S from biogas. *Sustainability* **2021**, *13*, 6262. [Crossref]
140. Pessôa, T. S.; Lima Ferreira, L. E. de; da Silva, M. P.; Pereira Neto, L. M.; Nascimento, B. F. do; Fraga, T. J. M.; Jaguaribe, E. F.; Cavalcanti, J. V.; da Motta Sobrinho, M. A.; Açaí waste beneficing by gasification process and its employment in the treatment of synthetic and raw textile wastewater. *Journal of Cleaner Production* **2019**, *240*, 118047. [Crossref]
141. Tejada, C. N.; Almanza, D.; Villabona, A.; Colpas, F.; Granados, C.; Caracterización de carbón activado sintetizado a baja temperatura a partir de cáscara de cacao (*Theobroma cacao*) para la adsorción de amoxicilina. *Ingeniería y competitividad* **2017**, *19*. [Crossref]
142. Bello, O. S.; Ahmad, M. A.; Adsorptive removal of a synthetic textile dye using cocoa pod husks. *Toxicological and Environmental Chemistry* **2011**, *93*, 1298. [Crossref]
143. Haq, A. U.; Saeed, M.; Usman, M.; Yameen, M.; Muneer, M.; Tubbsum, S.; A comparative sorption study of Cr^{3+} and Cr^{6+} using mango peels: kinetic, equilibrium and thermodynamic. *Green Processing and Synthesis* **2019**, *8*, 337. [Crossref]
144. Zhang, L.; Ren, Y.; Xue, Y.; Cui, Z.; Wei, Q.; Han, C.; He, J.; Preparation of biochar by mango peel and its adsorption characteristics of Cd(II) in solution. *RSC Advances* **2020**, *10*, 35878. [Crossref]
145. Yang, I.; Kwon, D.; Kim, M. S.; Jung, J. C.; A comparative study of activated carbon aerogel and commercial activated carbons as electrode materials for organic electric double-layer capacitors. *Carbon* **2018**, *132*, 503. [Crossref]
146. IBGE, Instituto Brasileiro de Geografia e Estatística. 2021. Produção agropecuária. Disponível em: <https://www.ibge.gov.br/explica/producao-agropecuaria/>. Acesso em: 08 de dezembro 2022.
147. CONAB, COMPANHIA NACIONAL DE ABASTECIMENTO. Acompanhamento da Safra Brasileira de Grãos, Brasília, DF, v. 9, safra 2021/22, n. 10 décimo levantamento, julho 2022.
148. Jiang, W.; Liu, X.; Wang, X.; Yin, Y.; Characteristics of yield and harvest index, and evaluation of balanced nutrient uptake of soybean in Northeast China. *Agronomy* **2019**, 9, 310. [Crossref]
149. Barbosa, K. L; Silva, J. D. S.; Santos, T. V.; Malta, V. R. D. S.; Santos-Rocha, M. S. R.; Almeida, R. M. R. G.; Pre-treatment of steam explosion, chemical and morphological characterization of sugarcane bagasse used for 2G ethanol production. *Revista Virtual de Química* **2020**, 12, 63. [Crossref]
150. Aguiar, A; Milessi, T. S.; Mulinari, D. R.; Lopes, M. S.; Costa, S. M.; Candido, R. G.; Sugarcane straw as a potential second generation feedstock for biorefinery and white biotechnology applications. *Biomass & Bioenergy* **2021**, 144. [Crossref]
151. Alarcon, R. T.; Lamb, K. J.; Bannach, G.; North, M.; Opportunities for the use of Brazilian biomass to produce renewable chemicals and materials. *Chemsuschem* **2021**, 14, 1, 169. [Crossref]
152. Koul, B.; Yakoob, M. Shah, M. P.; Agricultural waste management strategies for environmental sustainability. *Environmental Research* **2022**, 206, 112285. [Crossref]
153. Siqueira, M. U.; Contin, B.; Fernandes, P. R. B.; Ruschel-Soares, R.; Siqueira, P. U.; Baruque-Ramos, J.; Brazilian agro-industrial wastes as potential textile and other raw materials: a sustainable approach. *materials circular economy* **2022**, 4, 9. [Crossref]
154. Zhu, B.; Fan, T.; Zhang, D.; Adsorption of copper ions from aqueous solution by citric acid modified soybean straw. *Journal of Hazardous Materials* **2008**, 153, 300. [Crossref]
155. Xu, R.-K.; Xiao, S.-C. Yuan, J.-H.; Zhao, A.-Z.; Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. *Bioresource Technology* **2011**, 102, 10293. [Crossref]
156. Yin, Q.; Wang, R.; Zhao, Z.; Application of Mg-Al-modified biochar for simultaneous removal of ammonium, nitrate, and phosphate from eutrophic water. *Journal of Cleaner Production* **2018**, 176, 230. [Crossref]
157. Pan, J.; Jiang, J.; Xu, R.; Adsorption of Cr(III) from acidic solutions by crop straw derived biochars. *Journal of Environmental Sciences* **2013**, 25, 1957. [Crossref]
158. Wang, J.; Kang, Y.; Duan, H.; Zhou, Y.; Li, H.; Chen, S.; Tian, F.; Li, L.; Drosos, M.; Dong, C.; Joseph, S.; Pan, G.; Remediation of Cd^{2+} in aqueous systems by alkali-modified (Ca) biochar and quantitative analysis of its mechanism. *Arabian Journal of Chemistry* **2022**, 15, 103750. [Crossref]
159. Zeng, Y.; Li, W.; Wang, L.; Du, T..; Huang, J.; Huang, Z.; Wang, J.; Tang, J.; Wang, M.; Wang, J.; Jiang, C.; Yang, P.; Study on the kinetics of the adsorption of reactive brilliant red K-2BP onto modified soybean straw activated carbon. *Desalination and Water Treatment* **2018**, 125, 302. [Link]
160. Souza, P. R.; de Oliveira, A. C.; Vilsinski, B. H.; Kipper, M. J.; Martins, A. F.; Polysaccharide-based materials created by

physical processes: from preparation to biomedical applications. *Pharmaceutics* **2021**; 13, 621. [Crossref]

161. Giordano, E. D. V.; Brassesco, M. E.; Camiscia, P.; Picó, G. A.; Valetti, N. W.; A new alternative and efficient low-cost process for the removal of reactive dyes in textile wastewater by using soybean hull as adsorbent. *Water, Air and Soil Pollution* **2021**, 232, 165. [Crossref]
162. Honorio, J. F.; Veit, M. T.; Tavares, C. R. G.; Alternative adsorbents applied to the removal of natural hormones from pig farming effluents and characterization of the biofertilizer. *Environmental Science and Pollution Research* **2019**, 26, 28429. [Crossref]
163. Vidovix, T. B.; Januário, E. F. D.; Araújo, M. F.; Bergamasco, R.; Vieira, A. M. S.; Investigation of two new low-cost adsorbents functionalized with magnetic nanoparticles for the efficient removal of triclosan and a synthetic mixture. *Environmental Science and Pollution Research* **2022**, 29, 46813. [Crossref]
164. Cusioli, L. F.; Quesada, H. B.; Baptista, A. T. A.; Gomes, R. G.; Bergamasco, R.; Soybean hulls as a low-cost biosorbent for removal of methylene blue contaminant. Environmental *Progress and Sustainable Energy* **2020**, 39, 13328. [Crossref]
165. Arami, M.; Limaee, N. Y.; Mahmoodia, N. M.; Tabrizi, N. S.; Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull. *Journal of Hazardous Materials* **2006**, B135, 171. [Crossref]
166. Rizzuti, A. M.; Lancaster, D. J.; Utilizing soybean hulls and rice hulls to remove textile dyes from contaminated water. *Waste and Biomass Valorization* **2013**, 4, 647. [Crossref]
167. Módenes, A. N.; Hinterholz, C. L.; Neves, C. V.; Sanderson, K.; Trigueros, D. E. G.; Espinoza-Quiñones, F. R.; Borba, Ca. E.; Steffen, V.; Scheufele, F. B.; Kroumov, A. D.; A new alternative to use soybean hulls on the adsorptive removal of aqueous dyestuff. *Bioresource Technology Reports* **2019**, 6, 175. [Crossref]
168. Nunes, H. M. A. R.; Vieira, I. M. M.; Santos, B. L. P; Silva, D. P.; Ruzene, D. S.; Biosurfactants produced from corncob: a bibliometric perspective of a renewable and promising substrate. *Preparative Biochemistry & Biotechnology* **2021**, 52, 1. [Crossref]
169. Tang, S.; Chen, Y.; Xie, R.; Jiang, W.; Jiang, Y.; Preparation of activated carbon from corn cob and its adsorption behavior on Cr (VI) removal. *Water Science & Technology* **2016**, 73, 11. [Crossref]
170. Campos, N. F.; Guedes, G. A. J. C.; Oliveira, L. P. S.; Gama, B. M. V.; Sales, D. C. S.; Rodríguez-Díaz, J. M.; Barbosa, C. M. B. M.; Duarte, M. M. M. B.; Competitive adsorption between Cu^{2+} and Ni^{2+} on corn cob activated carbon and the difference of thermal effects on mono and bicomponent systems. *Journal of Environmental Chemical Engineering* **2020**, 8, 104232. [Crossref]
171. Alves, C. C.O.; Franca, A. S.; Oliveira, L. S.; Removal of phenylalanine from aqueous solutions with thermo-chemically modified corn cobs as adsorbents. *LWT - Food Science and Technology* **2013**, 51, 1. [Crossref]
172. Mohanty, S. S.; Kumar, A.; Biodegradation of Indanthrene Blue RS dye in immobilized continuous upflow packed bed bioreactor using corncob biochar. *Scientific Reports* **2021,** 11, 13390. [Crossref]
173. Tsade, H.; Abebe, B.; Murthy, H. C. A.; Nano sized Fe–Al oxide mixed with natural maize cob sorbent for lead remediation. *Material Research Express* **2019**, 6, 085043. [Crossref]
174. Younes, A. A.; Abdulhady, Y. A. M.; Shahat, N. S.; El-Dars, F. M. S. E.-D.; Removal of cadmium ions from wastewaters using corn cobs supporting nano-zero valent iron. *Separation Science and Technology* **2019**, 56, 1. [Crossref]
175. Wang, Y., Shen, F., Qi, X.; A corn stalk-derived porous carbonaceous adsorbent for adsorption of ionic liquids from aqueous solution. *RSC Advances* **2016**, 6, 32505. [Crossref]
176. García-Rosales, G.; Colín-Cruz, A.; Biosorption of lead by maize (*Zea mays*) stalk sponge. Journal of Environmental Management **2010**, 91, 2079. [Crossref]
177. Song, W.; Gao, B.; Zhang, T.; Xu, X.; Huang, X.; Yu, H.; Yue, Q.; High-capacity adsorption of dissolved hexavalent chromium using amine-functionalized magnetic corn stalk composites. *Bioresources Technology* **2015**, 190, 550. [Crossref]
178. Zheng, L.; Peng, D.; Meng, P.; Promotion effects of nitrogenous and oxygenic functional groups on cadmium (II) removal by carboxylated corn stalk. *Journal of Cleaner Production* **2018**, 201, 609. [Crossref]
179. Mousavi, S. A.; Kamarehie, B.; Almasi, A.; Darvishmotevalli, M.; Salari, M.; Moradnia, M.; Azimi, F.; Ghaderpoori, M.; Neyazi, Z.; Karami, M. A.; Removal of Rhodamine B from aqueous solution by stalk corn activated carbon: adsorption and kinetic study. *Biomass Conversion and Biorefinery* **2021**, *1*, 1. [Crossref]
180. Lima, D. R.; Klein, L.; Dotto, G. L.; Application of ultrasound modified corn straw as adsorbent for malachite green removal from synthetic and real effluents. *Environmental Science Pollution Research* **2017**, 24, 21484. [Crossref]
181. Xiao, L.; Bi, E.; Du, B.; Zhao, X.; Xing, C.; Surface characterization of maize-straw-derived biochars and their sorption performance for MTBE and benzene. *Environmental Earth Science* **2014**, 71, 5195. [Crossref]
182. Zhao, X.; Ouyang, W.; Hao, F.; Lin, C.; Wang, F.; Han, S.; Geng, X.; Properties comparison of biochars from corn straw with different pre-treatment and sorption behaviour of atrazine. *Bioresource Technology* **2013**, *147*, 338. [Crossref] [PubMed]
183. Anastopoulos, I.; Karamesouti, M.; Mitropoulos, A. C.; Kyzas, G. Z.; A review for coffee adsorbents. *Journal of Molecular Liquids* **2017**, 229, 555. [Crossref]
184. El-Azazy, Marwa; El-Shafie, A. S.; Morsy, H.; Biochar of spent coffee grounds as per se and impregnated with TiO_2: promising waste-derived adsorbents for balofloxacin. *Molecules* **2021**, 26, 2295. [Crossref]
185. Lessa, E. F.; Nunes, M. L.; Fajardo, A. R.; Chitosan/waste coffee-grounds composite: an efficient and eco-friendly adsorbent for removal of pharmaceutical contaminants from water. *Carbohydrate Polymers* **2018**, 189, 257. [Crossref]
186. Dai, Y.; Zhang, K.; Meng, X.; Li, J.; Guan, X.; Sun, Q.; Sun, Y.; Wang, W.; Lin, M.; Liu, M.; Yang, S.; Chen, Y.; Gao, F.; Zhang, X.; Liu, Z.; New use for spent coffee ground as an adsorbent for tetracycline removal in water. *Chemosphere* **2019**, 215, 163. [Crossref]

187. Cherdchoo, W.; Nithettham, S.; Charoenpanich, J.; Removal of Cr(VI) from synthetic wastewater by adsorption onto coffee ground and mixed waste tea. *Chemosphere* **2019**, 221, 758. [Crossref]
188. Ayala, J.; Fernández, B.; Treatment of mining waste leachate by the adsorption process using spent coffee grounds. *Environmental Technology* **2019**, 40, 2037. [Crossref]
189. Ferraz, F. M.; Yuan, Q.; Organic matter removal from landfill leachate by adsorption using spent coffee grounds activated carbon. *Sustainable Materials and Technologies* **2020**, 23, 141. [Crossref]
190. Pozo, C.; Rego, F.; Yang, Y.; Puy, N.; Bartrolí, J.; Fábregas, E.; Bridgwater, A. V.; Converting coffee silverskin to value-added products by a slow pyrolysis-based biorefinery process. *Fuel Processing Technology* **2021**, 214, 106708. [Crossref]
191. Ismail, S. A. A.; El-Anany, A. M.; Ali, R. F. M.; Regeneration of used frying palm oil with Coffee Silverskin (CS), CS Ash (CSA) and Nanoparticles of CS (NCS). *Journal of Oleo Science* **2017**, 66, 897. [Crossref]
192. Malara, A.; Paone, E.; Frontera, P.; Bonaccorsi, L.; Panzera, G.; Mauriello, F.; Sustainable exploitation of coffee silverskin in water remediation. *Sustainability* **2018**, 10, 3547. [Crossref]
193. Silva, W. R.; Costa, B. E. S.; Batista, A. D.; Alves, V. N.; Coelho, N. M. M.; Development of a disposable pipette extraction method using coffee silverskin as an adsorbent for chromium determination in wastewater samples by solid phase extraction. *Journal of the Brazilian Chemical Society* **2022***,* 33, 498. [Crossref]
194. Ayalew, A. A.; Aragaw, T. A.; Utilization of treated coffee husk as low-cost bio-sorbent for adsorption of methylene blue. *Adsorption Science & Technology* **2020**, 38, 205. [Crossref]
195. Castillo, N. E. T.; Sierra, J. S. O.; Oyervides-Muñoz, M. A.; Sosa-Hernández, J. E.; Iqbal, H. M. N.; Parra-Saldívar, R.; Melchor-Martínez, E. M.; Exploring the potential of coffee husk as caffeine bio-adsorbent – a mini-review. *Case Studies in Chemical and Environmental Engineering* **2021**, 3, 100070. [Crossref]
196. Oliveira, L. C. A.; Pereira, E.; Guimaraes, I. R.; Vallone, A.; Pereira, M.; Mesquita, J. P.; Sapag, K.; Preparation of activated carbons from coffee husks utilizing $FeCl_3$ and $ZnCl_2$ as activating agents. *Journal of Hazardous Materials* **2009**, 165, 87. [Crossref]
197. Castro, A. E.; Martinho, F. S.; Barbosa, M. L.; Franca, J. R.; Ribeiro-Soares, J.; Ferreira, G. M. D.; Ferreira, G. M. D.; Influence of methyl groups in triphenylmethane dyes on their adsorption on biochars from coffee husks. *Water, Air and Soil Pollution* **2022**, 233, 180. [Crossref]
198. Murthy, T. P. K.; Gowrishankar, B. S.; Prabha M. N. C.; Kruthi, M.; Krishna, R. H.; Studies on batch adsorptive removal of malachite green from synthetic wastewater using acid treated coffee husk: Equilibrium, kinetics and thermodynamic studies. *Microchemical Journal* **2019**, 146, 192. [Crossref]
199. Vu, N.-T.; Do, K.-U.; Insights into adsorption of ammonium by biochar derived from low temperature pyrolysis of coffee husk. *Biomass Conversion and Biorefinery* **2021**. [Crossref]
200. Laverde, M. P.; Salamanca, M.; Agredo, J. S.; Losada, L. M.; Palma, R. A. T.; Selective removal of acetaminophen in urine with activated carbons from rice (*Oryza sativa*) and coffee (*Coffea arabica*) husk: effect of activating agent, activation temperature and analysis of physical-chemical interactions. *Journal of Environmental Chemical Engineering* **2019**, 7, 103318 [Crossref]
201. Mimura, A. M. S.; Vieira, T. V. A.; Martelli, P. B.; Gorgulho, H. F.; Aplicação da casca de arroz na adsorção dos íons Cu^{2+}, Al^{3+}, Ni^{2+} e Zn^{2+}. *Química Nova* **2010**, 33, 6, 1279. [Crossref]
202. Ahmaruzzaman, M.; Gupta, V. K.; Rice husk and its ash as low-cost adsorbents in water and wastewater treatment. *Industrial & Engineering Chemistry Research* **2011**, 50, 13589. [Crossref]
203. Xiong, J.; Li, G.; Hu, C.; Treatment of methylene blue by mesoporous Fe/SiO_2 prepared from rice husk pyrolytic residues. *Catalysis Today* **2020**, 355, 529. [Crossref]
204. Pham, T.-D.; Le, T.-M.-A.; Pham, T.-M.-Q.; Dang, V.-H.; Vu, K.-L.; Tran, T.-K.; Hoang, T.-H.; Synthesis and characterization of novel hybridized CeO_2@SiO_2 nanoparticles based on rice husk and their application in antibiotic removal. *Langmuir* **2021**, 37, 2963. [Crossref]
205. Ma, J.; Li, T.; Liu, Y.; Cai, T.; Weid, Y.; Dong, W.; Chen, H.; Rice husk derived double network hydrogel as efficient adsorbent for Pb(II), Cu(II) and Cd(II) removal in individual and multicomponent systems. *Bioresource Technology* **2019**, 290, 121793. [Crossref]
206. Abaide, E. R.; Dotto, G. L.; Tres, M. V.; Zabot, G. L.; Mazutti, M. A.; Adsorption of 2–nitrophenol using rice straw and rice husks hydrolyzed by subcritical water. *Bioresource Technology* **2019**, 284, 25. [Crossref]
207. Herrera, K.; Morales, L. F.; Tarazona, N. A.; Aguado, R.; Saldarriaga, J. F.; Use of biochar from rice husk pyrolysis: part A: recovery as an adsorbent in the removal of emerging compounds. *ACS Omega* **2022**, 7, 7625. [Crossref]
208. Schwantes, D.; Gonçalves-Junior, A. C.; Coelho, G. F.; Campagnolo, M. A.; Dragunski, D. C.; Tarley, C. R. T.; Miola, A. J.; Leismann, E. A. V.; Chemical modifications of cassava peel as adsorbent material for metals ions from wastewater. *Journal of Chemistry* **2016**, 1, 1. [Crossref]
209. Schwantes, D.; Junior, A. C. G.; Perina, H. A.; Tarley, C. R. T.; Dragunski, D. C.; Junior, E. C.; Zimmermann, J. Ecofriendly; Biosorbents produced from cassava solid wastes: sustainable technology for the removal of Cd^{2+}, Pb^{2+}, and Cr^{total}. *Adsorption Science & Technology* **2022**, 2022, 1 [Crossref]
210. Alongamo, B. A. A.; Ajifack, L. D.; Ghogomu, J. N.; Nsami, N. J.; Ketcha, M. J.; Activated carbon from the peelings of cassava tubers (*Manihot esculenta*) for the removal of nickel(II) ions from aqueous solution. *Journal of Chemistry* **2021**. [Crossref]
211. EMBRAPA, Empresa Brasileira de Pesquisa Agropecuária, 2015. Disponível em: <https://www.embrapa.br/agrossilvipastoril/sitio-tecnologico/trilha-tecnologica/tecnologias/culturas/feijao>. Acesso em: 25 de Julho de 2022.
212. Sá, I. C.; Silva, P. M. O.; Nossol, E.; Borges, P. H. S.; Lepri, F. G.; Semaan, F. S.; Dornellas, R. M.; Pacheco, W. F.; Modified dry bean pod waste (*Phaseolus vulgaris*) as a biosorbent for fluorescein removal from aqueous media: Batch and fixed bed studies. *Journal of Hazardous Materials* **2022**, 424, 127723. [Crossref]

213. Bayomie, O. S.; Kandeel, H.; Shoei, T.; Yang, H.; Youssef, N.; El-Sayed, M. M. H.; Novel approach for effective removal of methylene blue dye from water using fava bean peel waste. *Scientific Reports* **2020**, 10, 7824. [Crossref]
214. Cabal, B.; Budinova T.; Ania, C. O.; Tsyntsarski, B; Parra, J. B.; Petrova, B.; Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods. *Journal of Hazardous Materials* **2009**, 161, 1150. [Crossref]
215. Gupta, K.; Gupta, D.; Khatri, O. P.; Graphene-like porous carbon nanostructure from Bengal gram bean husk and its application for fast and efficient adsorption of organic dyes. *Applied Surface Science* **2019**, 476, 647. [Crossref]
216. Raulino, G. S. C.; Silva, L. S.; Vidal, C. B.; Almeida, E. S.; Melo, D. Q.; Nascimento, R. F.; Role of surface chemistry and morphology in the reactive adsorption of metal ions on acid modified dry bean pods (*Phaseolus vulgaris* L.) organic polymers. *Journal of Applied Polymer Science* **2018**, 135, 45879. [Crossref]
217. Farooq, U.; Kozinski, J. A.; Khan, M. A.; Athar, M.; Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature. *Bioresource Technology* **2010**, 101, 5043. [Crossref]
218. Lewoyehu, M.; Comprehensive review on synthesis and application of activated carbon from agricultural residues for the remediation of venomous pollutants in wastewater. *Journal of Analytical and Applied Pyrolysis* **2021**, 159, 105279. [Crossref]
219. Banerjee, S.; Chattopadhyaya, M. C.; Uma; Sharma, Y. C.; Adsorption characteristics of modified wheat husk for the removal of a toxic dye, methylene blue, from aqueous solutions. *Journal of Hazardous, Toxic, and Radioactive Waste* **2014**, 18, 56. [Crossref]
220. Banerjee, S.; Gautam, R. K.; Jaiswala, A.; Gautam, P. K.; Chattopadhyaya, M. C.; Study on adsorption behavior of Acid Orange 10 onto modified wheat husk. *Desalination and Water Treatment* **2015**, 57, 1. [Crossref]
221. Bulut, Y; Baysal. Z.; Removal of Pb(II) from wastewater using wheat bran. *Journal of Environmental Management* **2006**, 78, 107. [Crossref]
222. Nameni, M.; Moghadam, M. R. A.; Arami, M.; Adsorption of hexavalent chromium from aqueous solutions by wheat bran. *International Journal of Environmental Science and Technology* **2008**, 5, 161. [Crossref]
223. Shen, Z.; Zhang, Y.; McMillan, O.; Jin, F.: Al-Tabbaa, A.; Characteristics and mechanisms of nickel adsorption on biochars produced from wheat straw pellets and rice husk. *Environmental Science and Pollution Research* **2017**, 24, 12809. [Crossref]
224. Ogata, F.; Nagai, N.; Itami, R.; Nakamura, T.; Kawasaki, N.; Potential of virgin and calcined wheat bran biomass for the removal of chromium(VI) ion from a synthetic aqueous solution. *Journal of Environmental Chemical Engineering* **2020**, 8, 103710. [Crossref]
225. Bulgariu, L., Bulgariu, D.J.; Functionalized soy waste biomass - a novel environmental-friendly biosorbent for the removal of heavy metals from aqueous solution. *Journal of Cleaner Production* **2018**, 197, 875. [Crossref]
226. Ma, H., Yang, J., Gao, X., Liu, Z., Liu, X., & Xu, Z.; Removal of chromium (VI) from water by porous carbon derived from corn straw: Influencing factors, regeneration and mechanism. *Journal of Hazardous Materials*, **2019**, 369, 550. [Crossref]
227. Pathak, U.; Das, P.; Banerjee, P.; Datta, S.; Treatment of wastewater from a dairy industry using rice husk as adsorbent: treatment efficiency, isotherm, thermodynamics, and kinetics modelling. *The Journal of Chemical Thermodynamics* **2016**, 3746316, 1[Crossref]
228. Ferraz, F. M.; Yuan, Q.; Organic matter removal from landfill leachate by adsorption using spent coffee grounds activated carbon. *Sustainable Materials and Technologies* **2020**, *23*, e00141. [Crossref]
229. Vu, N.-T.; Do, K.-U.; Insights into adsorption of ammonium by biochar derived from low temperature pyrolysis of coffee husk. *Biomass Conversion and Biorefinery* **2021**, 1. [Crossref]
230. Bandara, T.; Xu, J.; Potter, I. D.; Franks, A.; Chathurika, J. B. A. J.; Tang, C.; Mechanisms for the removal of Cd(II) and Cu(II) from aqueous solution and mine water by biochars derived from agricultural wastes. *Chemosphere* **2020**, *254*, 126745. [Crossref]
231. Abia, A. A.; Horsfall, M.; Didi, O.; The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. *Bioresource Technology* **2003**, *90*, 345. [Crossref] [PubMed]
232. Zwain, H. M.; Vakili, M.; Dahlan, I.; Waste material adsorbents for zinc removal from wastewater: a comprehensive review. *International Journal of Chemical Engineering* **2014**, *2014*, [Crossref].
233. Oyewo, O. A.; Onyango, M. S.; Wolkersdorfer, C.; Application of banana peels nanosorbent for the removal of radioactive minerals from real mine water. *Journal of Environmental Radioactivity* **2016**, *164*, 369. [Crossref]
234. Ahmad, T.; Danish, M.; Prospects of banana waste utilization in wastewater treatment: a review. *Journal of Environmental Management* **2018**, *206*, 330. [Crossref]
235. Etorki, A. M.; El-Rais, M.; Mahabbis, M. T.; Moussa, N. M.; Etorki, A. M.; El-Rais, M.; Mahabbis, M. T.; Moussa, N. M.; Removal of some heavy metals from wastewater by using of fava beans. *American Journal of Analytical Chemistry* **2014**, *5*, 225. [Crossref]
236. Yasdi, Y.; Ussarvi, D.; Rinaldi, R.; Juita, F.; Cahyani, S. E.; Coconut shell-based activated carbon preparation and its adsorption efficacy in reducing BOD from the Real Wastewater from Kitchen Restaurant (RWKR): characteristics, sorption capacity, and isotherm model. *Jurnal Presipitasi: Media Komunikasi dan Pengembangan Teknik Lingkungan* **2021**, *18*, 116. [Crossref]
237. Nandeshwar, S. N.; Mahakalakar, A. S.; Gupta, R. R.; Kyzas, G. Z.; Green activated carbons from different waste materials for the removal of iron from real wastewater samples of Nag River, India. *Journal of Molecular Liquids* **2016**, *216*, 688. [Crossref]