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Potential of agricultural and agroindustrial wastes as adsorbent materials of toxic heavy metals: a review

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ABSTRACT

Most of the population does not have water access with the required quality and quantity, because natural resources are adversely affected by anthropic activities. Agricultural and industrial activities result in the release of a high amount of contaminants into the environment, among these, toxic heavy metals are the ones that are of most concern to the society. These metals (Hg, Pb, Cd and Cr – for example) can be accumulated and bioaccumulated in the trophic chain. When high concentrations of these elements are in the human organism, metabolic, renal and blood dysfunctions, cancers, among others, can occur. Another increasing environmental problem is the high amount of agricultural wastes produced annually. Population growth generates an inelastic demand for food, and the production of these food results in an increasing amount of waste. The use of these wastes to produce adsorbents could add value to these residues. Moreover, the new adsorbents could be used in the decontamination of polluted waters containing toxic metals such as Hg, Pb, Cd, Cr and others. Also, these residues from agriculture could also be used to produce activated carbons, since activated carbons can adsorb more heavy metal than in natura material. Aiming to solve two environmental problems at once (the decontamination of heavy metals from waters and the correct destination of solid agroindustry wastes), this study investigated the capacity and viability of the decontamination of waters by the use of adsorbents produced from agroindustrial biomasses.

Keywords: Activated carbon; Heavy metals; Contaminated water; Toxic metals

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1. Introduction

About 70% of the Earth's surface is water-covered, however, only 0.002% of the water is available for human consumption. According to the World Health Organization (WHO), one-sixth of the world's population does not have access to drinking water. This is because industrial and agricultural source pollution negatively impacts this resource [1].

That is why drinking water sources, both superficial and underground, are increasingly degraded with coliforms, heavy metals and pesticides [2]. Since water is an essential environmental compartment for life on earth, the recovery/decontamination of these water compartments is of fundamental importance [3].

Among the contaminants that reach the aquatic environment, toxic metals are the ones that most present risks to fauna and flora, since it can be bioaccumulated in living tissues [4] causing injuries and disorders such as: cancer, stroke, anemia, digestive and renal disorders [5,6].

Non-essential metals are toxic to plant metabolism and have harmful effects on living beings [7]. Pb, Sb, Cr^{6+}, Co, Ag, Se, Hg, Cd and As, for example, are not suitable for biological functions and are potentially toxic, having toxic harmful or unknown biological and physiological functions [4,8].

Another increasing global problem is the increase of the volume of agricultural and agroindustrial waste, associated to the inadequate disposal. The recovery of these wastes is of fundamental importance, because it reduces the environmental impacts, protects the public health and allows to add value to the materials. One way of exploiting the adsorbents is related to the ability of some wastes to be used as alternative adsorbents in the efficient removal of contaminants in aquatic systems [9].

In this sense, the potential of several wastes has been extensively evaluated in the remediation of wastewater. Some materials with good potential for remediation of water contaminated by metallic ions are: pinus bark [10]; waste from the cassava industry [11]; jatropha biomass (*Jatropha curcas*) [12]; endocarp of açaí [13], canola genotypes [14, 15,16], among others.

Although the adsorption with in natura and chemically modified adsorbents has promising results, the transformation of these residues into activated carbon to remove the same contaminants, usually, is more effective and promising [17,18].

Commercial activated carbon is considered a good material for separating contaminants from wastewater, but it has a high cost [17,18]. In this sense, the production of activated carbon from agricultural residues has demonstrated efficiency and low-cost compared with industrial activated carbon, and furthermore, the removal of contaminants by alternative carbons can be higher than the in natura adsorbents produced by the same material [19–21].

Therefore, in order to study the resolution of two environmental problems at the same time, this study aimed (i) to investigate the capacity and feasibility of the decontamination of waters by adsorbents produced from agricultural and agroindustrial residues and also, (ii) to find a more adequate destination for these residues that have low added value, thus, allowing the remediation of water compartments.

2. Pollution of the aquatic system

Water is essential for all life on earth and the most important basis for all human activities [22]. However, human activities such as industrial development and agricultural activities generate high amount of effluents, which when disposed of inappropriately contaminate soils and aquatic systems. This is due to the high content of organic and metals in these industrial and domestic effluents [23].

Once contaminated by chemical residues (agricultural inputs, petrochemicals, pesticides and others), water bodies have a negative effect on the living organisms that live there, many contaminants are inserted in the trophic chain and can reflect on human health [1].

Among the main contaminants of the water bodies are heavy metals, which can be classified as essential, beneficial and toxic.

2.1. Insertion of heavy metals into the environment

Weathering is a geological process whose knowledge and use belongs to various spheres of human life, animals and plants, forming the substratum that together with water and air form the basis of life on earth.

The weathering of the rocks is the natural responsible for inserting metals into environmental compartments. This is an important process because many of these released metals are essential for fauna and flora. Generally, the toxic effect to plants and animals occurs due to the high amounts of metals released into the environment [25]. Although this contamination is sometimes natural [26], it usually occurs as a result of human activities – and not by this biogenic gradual release [25].

Heavy metal is the term used to define elements of the periodic table that have atomic densities greater than 5 g cm^3, such as lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu) and iron (Fe) [27].

Although metals are natural components of the aquatic environment, their levels have been increased due to the production of industrial waste, agricultural and mining activities, being one of the most serious problems in aquatic environments [28].

Once in the aquatic ecosystem, heavy metals constitute a serious environmental and human health problem, since many of these elements are stable, being more easily bioaccumulated, migrating from the components of the trophic chain. Among the metals, some can be toxic and accumulate in living tissues; this group has no known metabolic functions and can cause disorders in living beings [8].

2.2. Action of metals in living being

Few metals, such as Fe, Zn, Cu, Co, Cr, Mn, Mo, Mg and Ni, are required for biological metabolism in trace amounts [4,5,8], these metals are essential micronutrients necessary to catalyze the main enzymatic reactions [26], however, higher doses can also cause toxic effects [8].

At appropriate levels, these beneficial elements enhance plant nutrition and various mechanisms essential for plant growth and yield (growth, productivity), on the other hand, in excess they become toxic by changing the plant's physiological processes, and by changing the ability to absorb and accumulate other essential and non-essential elements [5].

The excess of metals cause direct effects in the plant, such as oxidative stress, which aggravates the inhibition of cytoplasmic enzymes and damage to cellular structures. Although direct effects are the substitution of essential nutrients at the cation exchange sites of the plant, these ions readily influence the role of various enzymes and proteins, disrupt metabolism and reveal phytotoxicity [5].

Non-essential metals are toxic to plant metabolism and have deleterious effects on enzymatic activity, photosynthetic properties, cell membrane, permeability and, eventually, plant growth.

For example Pb, Sb, Cr, Co, Ag, Se, Hg, Cd are not suitable for biological functions and are potentially toxic, having unknown biological and physiological functions [4,8,29]. And that is just one of the reasons why the toxicity of these elements is a considerable concern worldwide [8].

Unprecedented bioaccumulation and biomagnification of these elements in the environment have become a dilemma for all living organisms. Heavy metals at toxic levels have the ability to interact with several vital cell biomolecules, such as nuclear proteins and DNA, leading to the excessive increase of reactive oxygen species, resulting in severe morphological; metabolic and physiological anomalies in the plants; chlorosis from sprouting to lipid peroxidation and protein degradation [4].

Although all toxic metals are harmful to living being, it is possible to emphasize mainly Cd, Cr, Pb, As and Hg [30].

2.2.1. Cadmium (Cd)

With reduced availability in the earth's crust, cadmium (Cd) is commonly found in the form of impurity in deposits of other metals, such as Zn and Pb. Thus, Cd is mainly produced as a by-product of the Zn or Pb smelting [31].

This element is a highly toxic heavy metal that accumulates in the living being and is, therefore, one of the most important environmental and occupational pollutants. By reaching the environment by anthropogenic actions [32], due to the high soil-plant transfer rates, this toxic heavy metal into the trophic chain is mostly inevitable [33].

The accumulation and bioaccumulation in animals causes severe brain damage and neurotoxic effects [34]. Human absorption occurs through the ingestion of contaminated substances, by the consumption of tobacco [32] and by activities related to welding [31].

Although long-term ingestion of Cd causes an impact on many systems and organs, the kidney is considered a critical target because it is one of the organs most affected by its toxicity [33]. This occurs because it has an extremely long biological half-life (approximately 20–30 years in humans) and low rate of excretion of the body causes the storage of Cd predominantly in the soft tissues (mainly liver and kidneys) with a variety of toxic effects, such as nephrotoxicity, hepatotoxicity, endocrine and reproductive toxicities [32].

In addition, Cd contamination is associated with the development of renal dysfunctions, chronic kidney disease, hypertension, weight gain, zinc reabsorption, among others [33,35–37].

The solubility of Cd^{2+} relative to pH can be seen in the speciation diagram in Fig. 1 [38], where is observed that cadmium speciation have little soluble or insoluble forms in pH ranges higher than 9, with the formation of cadmium hydroxides, which have little availability in water or even soils.

2.2.2. Lead (Pb)

Lead (Pb) is a well-known toxic heavy metal, which even at low levels can cause serious risks to public health [39]; this metal is in its natural form in the environment with 87% purity (called galena), but has low availability when compared with other metals [40]. Although its toxicity has been recognized since the second century BC, Pb has been widely used since antiquity [41].

There was a lot of intoxication through the contamination of water carried by lead pipes in the 19th century; this type of plumbing was very common and carried drinking water to homes [42].

Another common use of Pb (and that is used until nowadays), was the addition in dyes, in this case the metal gains

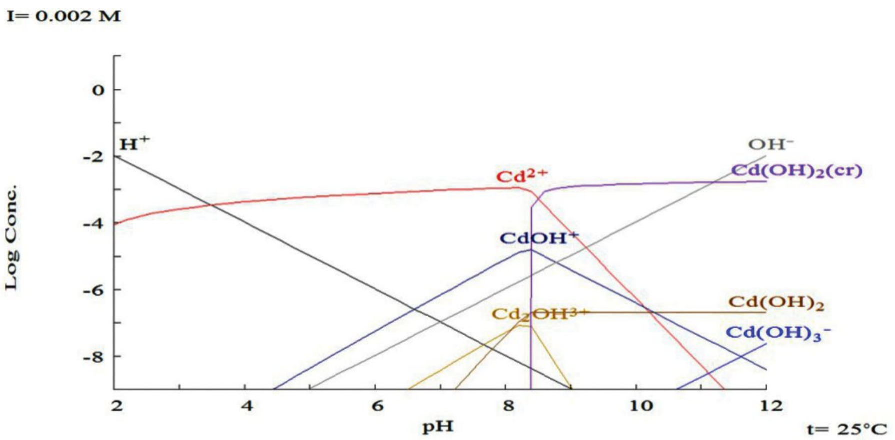

Fig. 1. Theoretical diagram for Cd species as a function of the pH obtained through the Hydra/medusa Software [38].

the function of pigment forming unique colorations. It is suspected that in the past centuries many artists have suffered death due to complications caused by direct contact with these pigments and dyes – which were more rustic compared with those produced in modern times [41].

More recently, in the twentieth century (1920–1970), tetraethyl lead was added to gasoline worldwide. After verifying the toxicities that this junction promoted in automotive engines, this element was slowly being removed from gasoline in several countries. Most countries have banned or restricted this addition, but there are countries that still use this addition (e.g., Afghanistan and North Korea). And in other countries, such as the United States of America, a small amount of tetraethyl lead is still being used in marine and aircraft engines [39].

The addition of Pb in gasoline promoted large-scale environmental contamination, Pb was released into the atmosphere by the exhaust pipe of automobiles, and because it was a dynamic environmental compartment, the atmosphere disseminated Pb, contaminating soil and water.

Nowadays, Pb is the most common toxic heavy metal in soil [19,43], their compounds remain stable for long periods, and they are hardly dissociated [19], due to the site stability and due to the complexity of the biological toxicity mechanism, its toxic effects cause severe environmental and health problems [44].

Although the general levels of population exposure to Pb have declined in recent decades, persistent exposure has occurred in the most deprived urban populations. This portion of the population is often exposed more easily to contaminated environment [45].

Often exposure to lead is also related to diseases such as diabetes [45]. Lead exposure represents risk to the entire population, but it is particularly dangerous for children, resulting in mental retardation when there is an abnormal concentration in the blood [44]. In this same group, concentrations above 40 μg dL^{-1} result in the blockade of hemoglobin synthesis, causing severe anemia [19].

Among the factors that affect the availability of Pb, the pH is the one with greater influence Pb availability in soil, water or any living organism. The solubility of Pb relative to pH can be seen in the speciation diagram in Fig. 2 [38].

It is observed that for pH values higher than 7, little soluble or insoluble forms of Pb hydroxides predominate.

2.2.3. Chromium (Cr)

Chromium (Cr) is a natural element found in rocks, animals, plants, soil and dust, and volcanic gases, occurring in different states of oxidation ranging from 2^+ to 6^+ [46]. However, in recent decades there has been an increase in the use of Cr in several anthropogenic activities [47].

Cr is used extensively in many industries including metallurgy, electroplating, paint and pigment production, tanning, wood preservation, chemical production and paper pulp production [48]. The increased use of Cr in these industrial activities, geological activities and land uses elevate the levels of metals in the environment [49].

Although Cr^{3+} and Cr^{6+} are stable, both differ significantly in their biological, geochemical and toxicological properties. Cr^{3+} occurs naturally in the environment at low concentration and is considered less toxic than Cr^{6+} [46].

Cr toxicity in plants depends on their valence state, Cr^{6+} is highly mobile and toxic, while Cr^{3+} is less mobile and toxic. The absorption of this metal by plants occurs by means of transporters of essential ions, such as sulfate [47].

Therefore, once in soil or water, Cr^{6+} can adversely affect the trophic chain [50]. However, translocation and accumulation depend on its speciation, which also conditions its toxicity to plants [47].

Once in water or soil, Cr is transformed by oxidations, reductions, sorption, desorption, precipitation and dissolution. While the solubility of Cr^{3+} is pH dependent, Cr^{6+} is extremely soluble at all pH conditions. And because it is a non-essential element for plants, it does not have any specific mechanism for its use [47].

The behavior of Cr^{3+} as a function of pH can be observed in Fig. 3, which shows that in more acidic environments soluble forms of Cr dominate, and, in more basic environments, insoluble complexes of the metal predominate [38]. The multiple compounds which can be found by the speciation of Cr in different pH ranges can be seen in Fig 3, where in pH ranges higher than 5, predominate Cr oxides and hydroxides, with low or no solubilization in water.

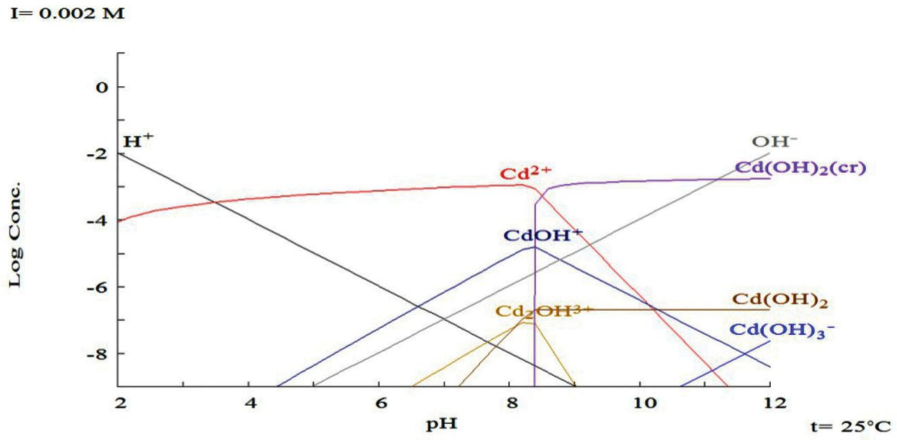

Fig. 2. Theoretical diagram for Pb species as a function of the pH obtained through the Hydra/medusa Software [38].

2.2.4. Arsenic (As)

In humans, the ingestion of high levels of arsenic can result in death. Exposure to lower levels can cause nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and a sensation of "pins and needles" in hands and feet. The ingestion of inorganic arsenic can increase the risk of skin cancer and cancer in the liver, bladder and lungs. Inhalation of inorganic arsenic can cause increased risk of lung cancer. Exposure to higher than average levels of arsenic occurs mostly in the workplace near hazardous waste sites or in areas with high natural levels of the metal. At high levels, inorganic arsenic can cause death [51].

According to the literature [52,53], the maximum permitted levels of As in soils is 14 mg kg^{-1} in the United States, 30 mg kg^{-1} in Poland, 20 mg kg^{-1} in Germany, 10 mg kg^{-1} in United Kingdom and 50 mg kg^{-1} in Austria.

Currently in Brazil, the legislation that deals about soil contamination is Resolution n°. 420 of 2009 of the National Council of Environment (CONAMA) [54], which aims to establish the criteria and values that guide of soil quality as the presence of chemical substances, among them toxic metals. The resolution establishes three categories of guiding values which are: The Reference Value Quality (RVQ) which is the concentration of a substance that will define the natural quality of the soil, based on previous studies for each Brazilian state, the prevention value (PV), which refers to the concentration limit of a substance in soil, and the investigation value (IV), which is the concentration of a substance in soil of which there are potential risks to human health [51].

By the Brazilian legislation, the prevention values (PV) for As in soils is 15 mg kg^{-1} and the investigation values (IV), is 35 mg kg^{-1} in agriculture areas, 55 mg kg^{-1} in residential areas and 150 mg kg^{-1} in industrial areas [54].

This element cannot be destroyed in the environment. It can only change its form, or become attached to or separated from particles. It may change its form by reacting with oxygen or other molecules in air, water, or soil, or by the action of bacteria that live in soil or sediment.

As is associated with ores containing metals, such as copper and lead, arsenic may enter the environment during the mining and smelting of these ores. Small amounts of arsenic also may be released into the atmosphere from coal-fired power plants and incinerators because coal and waste products often contain some arsenic [51].

As shown by the theoretical speciation of As in Fig. 4, this element can be part on the formation of different compounds, depending on the pH of the environment. The arsenic trioxide (As_2O_3) is slightly soluble in water when in its allotropic cubic form. Arsenic pentoxide (As_2O_5) is very soluble in water, 630 g of arsenic pentoxide dissolve in 100 g of water. In alkaline solution, anions such $AsO(OH)_2^-$, $AsO_2(OH)^{-2}$ and AsO_3^{-3} might be soluble. However, it has been claimed that the m-arsenite ion, AsO_2^-, can also be soluble in such solutions. It is generally agreed that trivalent arsenic is considerably more toxic than pentavalent arsenic, so the question of whether arsenic exists in aqueous media in the form of arsenite or arsenate – that is, AsO_3^{-3} or AsO_4^{-3} – is very important [55].

As, according to the Agency for Toxic Substances and Disease Registry [55] (CAS ID#: 7440-38-2) is a naturally occurring element widely distributed in the earth's crust. In the environment, is combined with oxygen, chlorine and sulfur to form inorganic arsenic compounds. In animals and plants, arsenic combines with carbon and hydrogen to form organic arsenic compounds. Inorganic arsenic compounds are mainly used to preserve wood. Copper chromated arsenic (CCA) is used to make "pressure-treated" lumber. CCA is no longer used in the United States for residential uses; it is still used in industrial applications. Organic arsenic compounds are used as pesticides.

2.2.5. Mercurium (Hg)

According to the literature [52,53], the maximum permitted levels of Hg in soils is 1–1.5 mg kg^{-1} in EU (European Union), 0.5 in the United States, 5 mg kg^{-1} in Poland, 2 mg kg^{-1} in Germany and 5 mg kg^{-1} in Austria.

By Brazilian legislation, the prevention values (PV) for Hg in soils is 0.5 mg kg^{-1} and the investigation values (IV), is 12 mg kg^{-1} in agriculture areas, 35 mg kg^{-1} in residential areas and 70 mg kg^{-1} in industrial areas [54].

According to the Agency for Toxic Substances and Disease Registry [56], mercury (CAS ID #: 7439-97-6) (Hg)

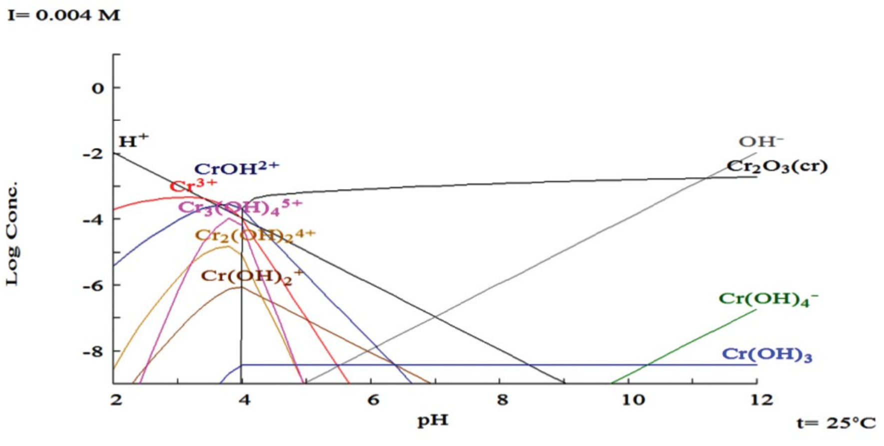

Fig. 3. Theoretical diagram for Cr species as a function of the pH obtained through the Hydra/medusa Software [38].

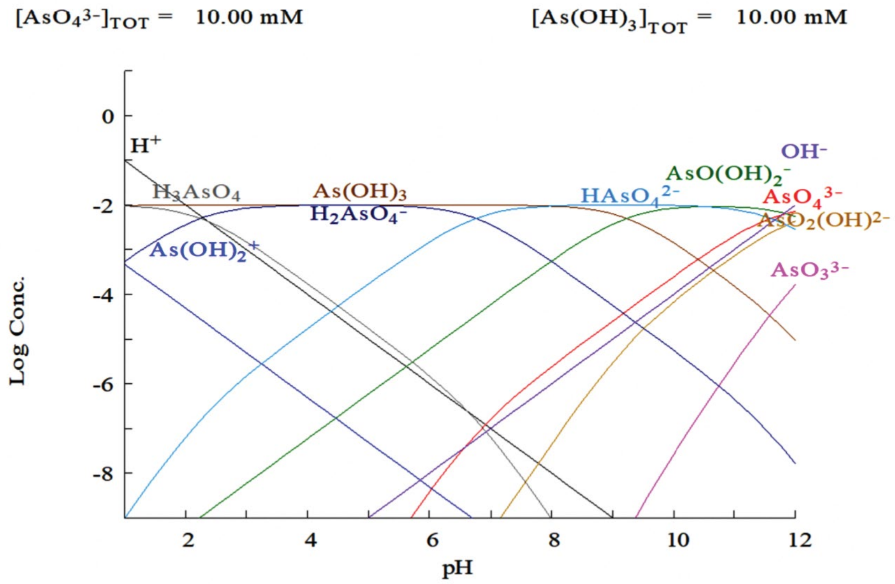

Fig. 4. Diagram of the As species as a function of the pH obtained through the Hydra/medusa Software [38].

is a naturally occurring metal. Metallic mercury is a shiny, silver-white, odorless liquid. When heated it becomes a colorless, odorless gas. Some of the health effects exposure to mercury may cause include irritation to the eyes, skin, and stomach; cough, chest pain, or difficulty breathing, insomnia, irritability, indecision, headache, weakness or exhaustion, and weight loss. Workers may be harmed from exposure to mercury. The level of exposure depends upon the dose, duration, and work being done.

Mercury is used in many industries. It is used to produce chlorine gas and caustic soda, and in thermometers, barometers, batteries, and electrical switches. Some examples of workers at risk of being exposed to mercury include the following [56]:

- Workers in facilities where electrical equipment is manufactured;
- Workers in fluorescent light bulb (CFL) recycling facilities;
- Workers in facilities where automotive parts are manufactured;
- Workers in chemical processing plants that use mercury;
- Workers in medical, dental, or other health services who work with equipment that contains mercury;
- Dentists and their assistants when breathing in mercury vapor released from amalgam fillings.

In more acidic pH ranges, Hg_2^{2+}, Hg^{2+}, Hg_2OH^+ and $HgOH^+$ forms predominate; while in pH ranges closer to neutrality to more alkaline pH, the $Hg(OH)_2$, $Hg_2(OH)_2$ (s) forms predominate (Fig. 5). In environment, a small portion of the Hg^0 that reaches the atmosphere is converted into water-soluble species (probably Hg^{2+}), which can be re-emitted to the atmosphere as Hg^0, through deposition in soil or exchange at the air/water interface [56].

Hg affects the following organ systems: Developmental (effects during periods when organs are developing), neurological (nervous system), renal (urinary system or kidneys).

2.3. Remediation of contaminated water

Water is the most essential environmental compartment for the survival of living beings because its quality and quantity directly and indirectly affect all ecosystems. For this reason, the study of water resources is of fundamental importance for the maintenance of life on the planet [57].

However, population growth has driven the use and transformation of raw materials into materials useful to supply human needs. This results in high growth in the agricultural and industrial sectors, resulting in a high load of wastewater [8]. When released inappropriately and/or indiscriminately into the environment, wastewater can negatively impact water resources – constituting point or diffuse contaminations [58].

Among the contaminants that most negatively affect water bodies are heavy metals. Among these, toxic metals such as Pb, Cd, Cr, As and Hg are among the most damaging to aquatic biota. Once in the water course, these metals are easily inserted into the trophic chain web and can reach humans [23].

However, increasing water consumption and high levels of pollution have generated a prominent need to manage water quality [57]. Usually decontamination methods of contaminated water are costly [3], so during the last decades, scientists have been trying to develop cheap environmental technologies for the treatment of domestic or industrial wastewater [8], trying to find ways to bypass the high cost adsorption technologies [3].

In this sense, methods such as ion exchange, membrane filtration, catalysts including photocatalysis, phytobioremediation associated with microorganisms, adsorption with biosorbents, low-cost nanomaterials [8] and use of degrading bacteria, have been studied [57].

Among these methods, the separation and purification of wastewater generated by adsorption phenomena are gaining great relevance. In addition to adding value to residual biomass, the adsorption capacity of biosorbents and activated

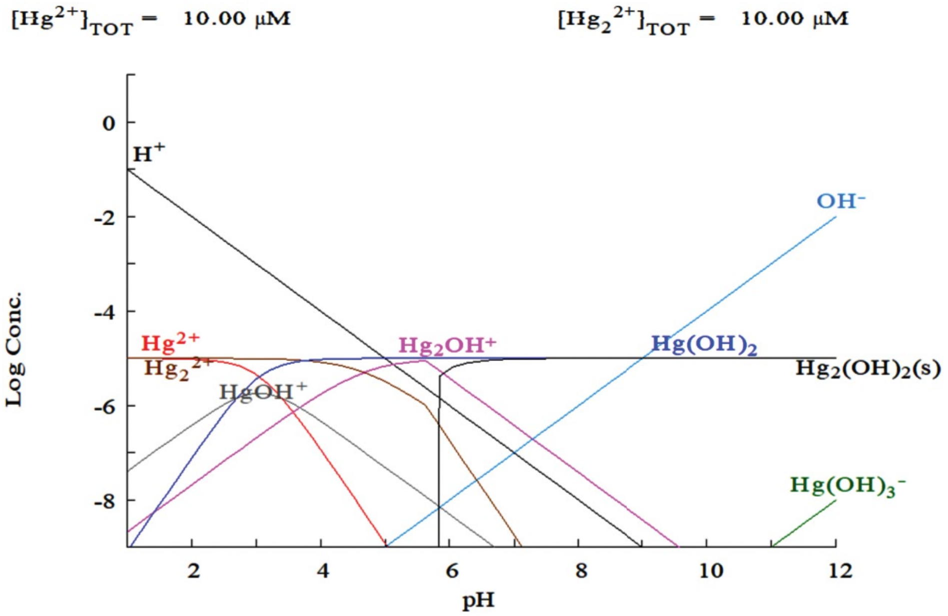

Fig. 5. Diagram of the Hg species as a function of the pH obtained through the Hydra/medusa Software [38].

carbon derived from this biomass provides the capacity to treat large-scale wastewater [8].

2.4. Adsorption

Being one of the most important treatment methods for the removal of pollutants from water and wastewater [17], adsorption techniques are widely used to remove pollutants [59]. It is a process of transferring material from a fluid phase to a solid phase. It is a separation process in which some materials (adsorbate) are concentrated from a bulk vapor or from a liquid phase to the surface of a porous solid (adsorbent) [60].

Adsorption is an effective method to remove toxic substances resulting from the release of industrial waste, being this one of the greatest challenges that the environment and society faces today [3].

The adsorption of metal ions may occur predominantly in the physical or chemical form. The physical adsorption is also called nonspecific adsorption, which occurs as a result of the long range of Van der Waals weak forces between adsorbent and sorbate, whereas the energy released when a particle is adsorbed physically is of the same magnitude as the condensation enthalpy [61].

The chemical adsorption (or chemisorption) occurs by ionic or covalent bond process, in which case high amounts of energy are required. The ion exchange property is the main method of chemical adsorption, generally depending on the chemical affinity between adsorbent and adsorbate, and not depending on the net surface charge, or surface functional groups [62,63].

2.5. Adsorbents

Due to the economic crisis of the 2000s, several researches started to investigate the use of solid wastes to adsorb contaminants [64]. Among the evaluated materials are agricultural residues, industrial solid waste, biomass, clay minerals and zeolites [59]. Among these, agricultural adsorbents have received much attention for their adsorption capacity of pollutants such as heavy metal ions and dyes [59]. Some of these are shown in Table 1.

Although they are used to adsorb a variety of contaminants, the evaluation of the removal of dyes, heavy metals, phenols, pesticides and pharmaceutical products is more common by means of adsorption processes than other contaminants; this is due to the environmental risk associated with these contaminations, and due to the high cost of treatment systems that aim the removal of these pollutants [64].

These researches shown in Table 1 state that the use of raw material (solid wastes) from distinct agroindustries can be used for the development of biosorbents, which are used in the removal of many contaminants (especially metals and dyes) from waters. This can be an excellent opportunity for undeveloped countries, such some in Latin America or Africa, in locations where water and wastewater treatment systems do not exist, or are precarious, or even in new industries in those countries, where these materials can be used in some specific parts of the water or wastewater treatment system.

Also, several modifications have been investigated in an attempt to improve the adsorption properties, as well as to improve the mechanical and physical characteristics of the low-cost adsorbents. Among these techniques, we can enumerate the processes of biomass modification as: grafting of monomers, photografting, high energy radiation grafting, chemical initiation grafting, direct chemical modifications (esterification, halogenation, oxidation, etherification, alkaline treatment, silylation treatment, etc.), and also the thermal, chemical and physical transformation through the production of activated charcoal [9–15,18–20,59,62,67,68].

Table 1
Adsorbents evaluated to remove contaminants from polluted waters

Authors	Precursor material	Adsorbents evaluated	Removal of:	Final characteristics predominant in adsorbent and results obtained
Schwantes et al. [11]	Cassava industry wastes	Activation with sulfuric acid – H_2SO_4 (I), sodium hydroxide – NaOH (II), hydrogen peroxide – H_2O_2 (III) and in natura (IV)	Cd, Pb and Cr	Material predominantly microporous, with good adjustments of isotherms for mono and multilayer
Schwantes et al. [10]	Pinus bark	Activation with H_2SO_4 (I), NaOH (II), H_2O_2 (III) and in natura (IV)	Cd, Pb and Cr	Chemically modified adsorbents demonstrated better removals for biomass in natura. The modification with H_2SO_4 resulted in a higher Pb, Cd and Cr removal capacity, with predominance of monolayer adsorption
Gonçalves Jr et al. [13]	Endocarp of açaí	Adsorbent in natura	Cd, Pb and Cr	Adsorption mainly in monolayer with strong interactions between adsorbent surface and metallic ions.
Al-Senani and Al-Fawzan [3]	Origanum and Lavandula	Adsorbent in natura	Cu and Ba	Viable, spontaneous and endothermic adsorption with mono and multilayer adsorption for both wild grasses.
Feizi and Jalali [15]	Agricultural wastes	Wastes of canola in natura (I), sunflower in natura (II), potato in natura (III) and nut shells in natura (IV)	Fe, Mn, Zn, Ni, Cu and Cd	Among the adsorbents, the residues of sunflower, potato, canola and nut shells reached high efficiency in the removal of Cd, Cu, Zn, Mn and Fe from aqueous solutions. Predominance of monolayer adsorption occurred.
Choi and Yu [65]	Agricultural wastes	Rice husk (I), rice straw (II), water hyacinth (III) and coconut shell (IV)	Fe from groundwater	Application of four rice husk plates achieved the allowance value and resulted in a final iron removal near of 70%.
El-Azazy et al. [66]	Agricultural by-product corncobs	Agricultural by-product corncobs in natura	Methylene blue	As a result of the experiment, MB concentration of less than 0.005 g L^{-1} was very efficiently removed with 10 g L^{-1} of bioadsorbent corncob and the maximum adsorption capacity of corncob for methylene blue dyes was obtained at 417.1 mg g^{-1}.
Islamuddin et al. [67]	Potato peels	Raw potato peel and potato peel burnt	Cd, Co, Cu, Fe, La, Ni and Pb	Large amount of micropores and mesopores with high adsorption capacity.

All these modifications provoked in the residual biomass aim for the increasing the potentiation of the precursor material as adsorbent. It has the intention to promote greater porosity and surface area to the material, in order to create characteristics more favorable to adsorption [68].

2.5.1. Biosorbents characterization

According to several authors [69–72], the biomass of different vegetal residues has characteristics that make them favorable to the development of natural or modified adsorbents, and these materials can be used in the removal of different metals from contaminated water. The observed structures of distinct biomass waste from vegetal origin (Fig. 6) directly demonstrate the micro-structures of different adsorbents.

The cavities structures of these vegetal materials reveal an adsorbent surface with lamellar, spongy, irregular and heterogeneous structure which, according to many authors [69–72] and others, can favor the adsorption of pollutants, especially metal ions in water solution.

In Table 2 it can be observed that the biosorbents originated from biomass of different plants have in their characterization different functional clusters, which are suitable for the sorption process of pollutants (especially metals, according to mentioned citations) from liquid medium.

2.6. Activated carbon

Activated carbon is the nomenclature given to the pyrolyzed material obtained in controlled conditions of high temperatures and under the influence of an activating agent [87].

Commercial activated carbon is considered a competitive and efficient material (gold standard) to separate contaminants from domestic and industrial water and wastewater, but its high cost has generated in recent years a growing interest in producing low-cost adsorbents [17,18]. Thus, many researchers have begun to study alternative adsorbents using low-cost materials such as agricultural waste [3].

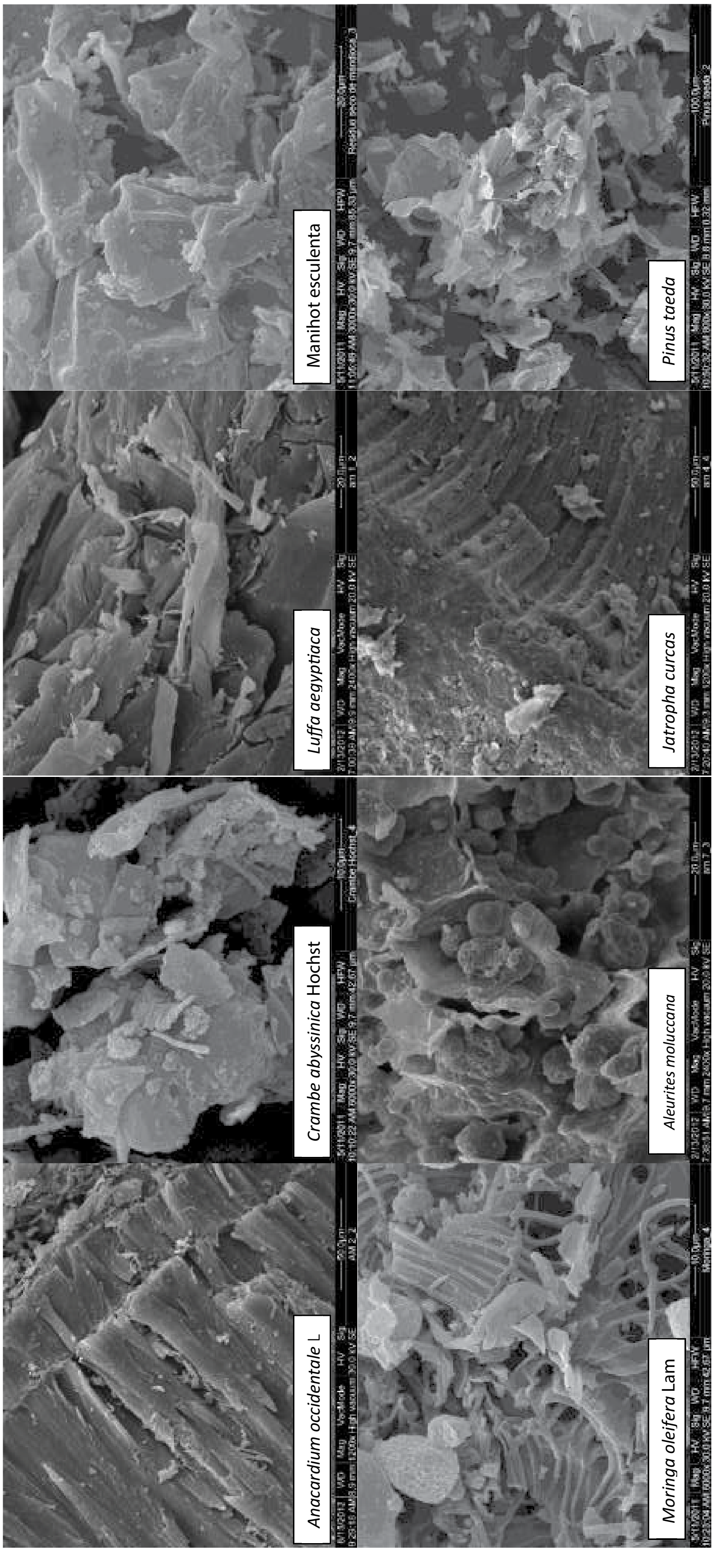

Fig. 6. MEV of Cashew nut shell *Anacardium occidentale* L (1,200×), *Crambe abyssinica* Hochst (6,000×), *Luffa aegyptiaca* (2,400×), Cassava barks (*Manihot esculenta*) [73] (3,000×), grains of *Moringa oleifera* Lam (6,000×), Nogueira de Iguape (*Aleurites moluccana* (L.) Willd); Euphorbiaceae) (2,400×), jatropha fruit wastes (*Jatropha curcas*) (2,400×), *Pinus taeda* (800×).

Table 2
Summary of infrared spectra observed in natural biosorbents proposed by several authors and developed from grape residue [74], *Jatropha curcas* L. fruit waste [72], solid residues of cassava roots [73], crambe cake [70], residues of the cashew nut shell *Anacardium occidentale* L. [69]

Approx. wavelength	Bonds or peaks		Cited references	Article where the data is observed
around 2,919 to 2,922 cm^{-1}	C–H bonds	Suggests the presence of alkanes, acyl, aliphatic acids and lipids	[75]	Grape residue [73]
around 3,395 to 3,422 cm^{-1}	Hydroxyl OH groups	Suggests the presence of water and cellulose	[76]	and
	N–H bonds	Suggests the primary (aliphatic and aromatic) and secondary amines in organic molecules		Crambe cake [70]
around 1,735 to 1,738 cm^{-1}	C=O bonds	May be aldehydes and esters groups, originating from polysaccharide, lipid and hemicellulose	[76]	
around 1,614 to 1,622 cm^{-1}	C–C	May be the phenyl ring stretch or acids peaks due to carbonyl and carboxyl groups	[77]	
around 1,513 to 1,522 cm^{-1}	N–H group	Suggests the secondary amide, probably of protein degradation	[78]	
around 1,441 to 1,443 cm^{-1}	C–H$_2$ or C–H$_3$	Related to lipids and fatty acids, and aromatic compounds, respectively	[76]	
around 1,390 cm^{-1}	C	May be carbon particles	[78]	
around 1,400 cm^{-1}	$-CH_3$ or $-CH_2$	May be methyl and methylene groups of proteins, lipids and amino groups being a symmetric bending mode of CH$_3$	[78]	
peaks around at 1,500 cm^{-1}	Carotene	Can be related to the presence of a carotenoid structure, a cellular pigment	[78]	
around 3,400 cm^{-1}	Hydroxyl links OH	Usually found in carbohydrates, fatty acids, proteins and other organic molecules lignin units, cellulose, alcohols, and adsorbed water	[79,80,81]	*Jatropha curcas* L. fruit waste [72]
around 2,900 cm^{-1}	Vibration lengthening of C–H	Suggests alkane and aliphatic groups	[82]	and Cashew nut shell
Peaks at 1,650, 1,542 and 1,370 cm^{-1}	Vibration lengthening of C–O	Type links in amides and carboxyl groups	[80]	*Anacardium occidentale* L. [69]
around 1,650 cm^{-1}	C=O-type links	Suggests carbonyl and carboxylate groups in lignin-cellulose	[83]	
Peaks at 1,542 and 1,370 cm^{-1}	C=C links	Links of aromatic compounds	[84]	
around 1,370 cm^{-1}	C–H	Cellulose, hemicellulose, and lignin links	[85]	
around 3,440–3,330 cm^{-1}	O–H	May be attributed to the stretching vibration of the O–H bond	[78,80,81]	Cassava biosorbents [73]
around 2,920 cm^{-1}	C–H	Suggests alkane groups	[76]	
around 1,730 cm^{-1}	Starch or carbonyl	Suggests starch or carbonyl from aldehyde functions in lignin and holocellulose	[86]	
Peaks at 1,420 and 1,650 cm^{-1}	C–O bonds	Amide and carboxylic groups	[80]	

In this sense, the production of activated carbon from agricultural residues has demonstrated efficiency and low-cost compared with industrial activated carbon, and in addition, the removal of contaminants by alternative carbon has been (often) higher than in natura adsorbents produced from the same material.

So, to produce a low-cost activated carbon, it is first necessary to choose a low-cost–waste biomass for transformation into activated carbon. It is possible to use, for example, material that has low or no added value, such as orange peel [88], winemaking wastes: bagasse and cluster stalks [89], coconut shells [90] and waste tea [19].

The high removal efficiency occurs, mainly due to the fine porous structure of the activated carbon and its extremely high surface area (can be > 1,000 $m^2 g^{-1}$), these characteristics result in powerful adsorption properties in gaseous or liquid phases [91–93].

Activated carbons can be obtained in several ways, and their final characteristics can (or cannot) resemble their precursor material, that depends on the used processes during the production of the same. The pyrolysis can be carried out before or after the activation process. Also, the activation can be either physical or chemical [20,94].

Once produced, the activated carbon can be used for a variety of purposes. Among the most commonly used uses, are the purification of water for human consumption, removal of industrial dyes, turbidity and solids of industrial and domestic effluents [95] and to treat manure – in order to remove color and odor and some heavy metals [91].

Although less frequent, the literature also cites the use of activated carbon for air purification, chromatography, energy storage, electrode materials for lithium battery biosensors, hydrogen storage, in the immobilization of biomolecules [93] and in the removal of toxic materials, substances, poisons introduced into the digestive system – stomach and intestine [91].

After the use of activated carbon in waters, it is common to adjust or improve parameters such as pH, turbidity, chemical oxygen demand, total dissolved solids and total suspended solids [21].

Many factors interfere in the final yield of the activated carbon; therefore, the variation of parameters can be studied extensively. Some parameters that can be evaluated are as follows:

- Precursor material chosen [88];
- Activation temperature [19];
- Activation: chemical or physical [90];
- Concentration of the chemical reagent [92];
- Activation combination chosen (when more than one activation is used for the same adsorbent) [92];
- Contact time between the precursor material and the activator [19,92];
- Pyrolysis temperature and time [19,88,89].

When using only the temperature at controlled burning, the resulting material is called "biochar" or "bio-carbon". Both materials (biochar and activated carbon) can be produced from the same raw material, resulting in distinct efficiency results [87].

In addition, the activation of carbon can be chemical or physical. Physical activation is a two-step process, first occurs the controlled burning of the precursor material, in a second moment the resulting carbon is activated in the presence of physical activators, such as water vapor, CO_2 and/or oxygen, or a mixture of these oxidizing gases [94,95].

Chemical activators are intended to raise the surface area of activated carbon by increasing its porosity [19]. This chemical activation of precursor material can occur in different ways. The material can be impregnated before or after pyrolysis [20].

Different bases, acids, oxides and salts can be used for this purpose; each of these materials gives the activated carbon different characteristics. The final characteristics can relate to both the precursor material and the used activating reagent. Some precursor materials that have been activated in different ways are described in Table 3.

Cost is supposedly the most subtle characteristic to understand because it may differ from day to day and from sales rep to sales rep, even for the same exact material. The cost of adsorption process is mainly dependent on the cost of adsorbent used for the metals removal from water or wastewater. In this way, low-cost materials, or active carbons obtained from these are economic feasibility and should be locally available [105].

For example, Ali et al. [105] state that the Egyptian peanut hulls, in Egypt, are generally available and abundant at a relatively cheap rate, 800 Egyptian pounds per ton. According to the authors, the finished products would cost approximately 2,000 Egyptian pounds per ton, including all expenses (peanut hulls, electrical energy, handling, transportation, chemicals, drying, etc.).

Gupta and Babu [106] studied the economic feasibility of low-cost adsorbents (especially, activated tamarind seeds, activated neem leaves and the sawdust and activated fly ash) for the removal of Cr(VI) from wastewater in India. According to them, sawdust is cheap and available in abundance in India, being the most economical adsorbent among all the developed and studied low-cost adsorbents, and much cheaper than activated carbon.

According to Gupta and Babu [106], the cost for the removal of 1 g of Cr(IV) from wastewater by activated tamarind seeds is 1.276 Rs (Indian rupee), 1.289 Rs by activated neem leaves, 0.105 Rs for sawdust, 1.640 Rs for activated fly ash and 6.97 Rs by activated carbon (traditional adsorbent).

Banerjee et al. [107], evaluating the Indian walnut production costs, state that in the year of 2017–18 India produced around 34,000 metric tons of walnut shell. So the adsorbent developed by Banerjee et al. [107] would locally be available at the rate of $ 385 per metric ton. The cost of adsorbent required per month was calculated considering 6 d per week and one adsorbent bed was used for three times. As the cost of adsorbent is very less, small and medium-scale industries will be capable of using this proposed treatment method.

Although the economic analysis from different parts of the world have variations in the economical analysis regarding the use of agroindustry residues for the production of adsorbents, one thing is quite sure, almost all of the authors state that by using agricultural by-products or/wastes as a low-cost adsorbent or as active carbon, financial benefits are obtained for the company [108].

According to Ali et al. [105], among the many environmental benefits from heavy metals removal from wastewater using adsorbents from agroindustry wastes are the possibility of treating wastewater without ecosystem damaging and to produce high quality of refined water that can be used in different purposes.

Another important factor of these new adsorbents is the possibility of its use in many adsorption cycles, which is very important, especially when it comes to the sustainability of

Table 3
Different precursor materials and activations in the production of activated carbon produced from agricultural and agroindustrial residues

Authors	Precursor material	Adsorbents evaluated	Pollutant	Final characteristics predominant in carbons
Fazal-Ur-Rehman [92]	Municipal organic solid waste (MOSW)	MOSW activated with H_3PO_4 30% (I), H_3PO_4 40% (II) and H_3PO_4 50% (III)	Methylene blue dye, Pb and Cd	Activated carbon with predominance of mesopores. Surface area of up to 792.97 $m^2\ g^{-1}$, the precursor material generated 32% of its weight in activated carbon. The authors achieved 100% dye removal. While the Cd and Pb removals reached up to 55% and 66%, respectively.
Alkhatib and Alzaailay [90]	Coconut shells	Coconut shells activated with $ZnCl_2$ (I), H_3PO_4 (II) and KOH (III) (concentrations = 0.3, 0.5, 0.67, 1.00 Mol L^{-1})	Methylene blue dye	H_3PO_4 (0.67 M) had the best adsorbent performance and absorbance. All activators increased ash and moisture content and decreased volatile constituents.
Sales et al. [96]	Banana peels	Banana peels activated with HCl (1 mol L^{-1})	Pb, Cd and Cr	High efficiency in the removal of Pb, Cd and Cr.
Sanni et al. [89]	Winemaking wastes – bagasse and cluster stalks	KOH	Methylene blue dye	High pore volume (0.8–1.4 $cm^3\ g^{-1}$) and texture dominated by micropores (<2 nm), but with presence of mesopores. The adsorption was spontaneous, exothermic and predominantly monolayer.
Alcaraz et al. [88]	Orange peel	H_2SO_4 – proportion 1:1 (m/v)	*	Extremely high surface area reaching 1,934 $m^2\ g^{-1}$.
Tadda et al. [94]	Piaçava of Amazônia (*Leopoldinia piassaba*)	Native piassava (I) Activated carbon (AC) native piassava (II) AC corona piassava (III), AC mercerized piassava (IV) and AC extractive-free piassava (IV)	Methylene blue dye	Predominance of micropores, and surface area up to 803.8 $m^2\ g^{-1}$. Pretreatment was effective, improving the properties of AC when compared with AC of untreated fibers. Homogeneous surface with good adsorption in monolayer.
Sales et al. [96]	Coco-da-baia mesocarp	Fibers of coco-da-baia mesocarp activated for 2 h in H_3PO_4 at a ratio of 90% (H_3PO_4 mass/fiber mass)	Hardness, chloride and acidity	Occurred reduction of 50% in the hardness, 87.5% in chloride and 66.6% in acidity on wastewater of the water treatment plant.
Özsin et al. [97]	Chickpea (*Cicer arietinum*) husks	Chickpea chemically activated with KOH (I) and chickpea chemically activated with K_2CO_3 (II).	Pb, Cu and Cr	Was observed significant differences between the surface topography of raw husk and produced carbons. The surface area of the chemically prepared AC from chickpea husk was relatively high, ACs prepared with both KOH and K_2CO_3 have a sponge-like porous structure with interconnected channels.
Zhou et al. [19]	Waste tea	Waste tea with physical activation by steam	*	The specific surface area and micropore volume increased with increases in activation temperature, as additional volatile materials were released.
Conradi Jr. et al. [98]	Tobacco from smuggled cigarettes	Tobacco in natura (I), carbon activated with NaOH (II) and with $ZnCl_2$ (III)	Pb	The use of chemical activation with NaOH and $ZnCl_2$ caused significant changes in the tobacco in natura, producing transformations on the surface of the adsorbents, suggesting the formation of new groups in the activated carbon. It causes a potential increase in the surface area of the activated carbons, 283 times for NaOH (II) and 1,775 times for $ZnCl_2$ (III) in comparison with the precursor material.

Ratan et al. [99]	Rice husk, corncob and wheat straw	Rice husk activated with NaCl (I), corncob activated with NaCl (II) and wheat straw activated with NaCl (III)	Methylene blue	The results showed that agricultural wastes can be used to produce low-cost adsorbents using a simple method. These adsorbents have potential for purification of drinking water in remote areas. The adsorption experiments showed good capacity of the prepared activated carbons for adsorption of methylene blue. The equilibrium data for adsorption of methylene blue fitted well into Langmuir isotherm.
Ravichandran et al. [100]	*Casuarina equisetifolia* fruit waste	Activation with H_3PO_4 (I), $ZnCl_2$ (II) e KOH (III)	Methylene blue, iodine and molasses	The carbon yield, BET surface area, removal of pollutants from liquid media (methylene blue, iodine and molasses) was found to be higher in the case of ACs produced from H_3PO_4 and KOH activating agents and two-step pyrolysis, than those produced by the one-step process and using $ZnCl_2$ activating agent.
AL-Othman and Naushad [101]	Peanut shell	Chemical activation with KOH (oxidized adsorbent)	Cr(IV)	Average pore width = 141.5 Å; micropore volume = 0.09 $cm^3\ g^{-1}$; pore diameter (BJH) = 115.10 Å; surface area (BJH) = 133.31 Å. The removal of Cr(IV) was higher for the oxidized carbon of peanut shell.
AL-Othman and Naushad [101]	Peanut shell	Chemical activation with KOH (unoxidized)	Cr(IV)	Average pore width = 142.84 Å; micropore volume = 0.08 $cm^3\ g^{-1}$; pore diameter (BJH) = 114.27 Å; surface area (BJH) = 129.89 Å. The removal of Cr(IV) was higher for the oxidized carbon of peanut shell.
Ghasemi et al. [102]	Ash and n-FeA using *Rosa canina* L. leaves	For ash: carbonized of biomass at 450°C. For n-FeA: chemical activation with $FeCl_3$ and pH correction with NaOH.	Pb	Ash: mainly constituted of compact or hollowed spheres of different size and some unshaped fragments. n-FeA: Fe nanoparticles were coated on the surface of ash. For both adsorbents, FIIR reveals OH, Si–OH groups. C=O stretching of carboxylic acid. $–CH_3$ groups, Si–O–Si, –C–O–H stretching and –OH deformation.
Yahya et al. [103]	Desiccated coconut residue	Chemical modification with KOH impregnation	Adsorption of contaminant not evaluated	The ideal conditions for adsorbent preparation were: 500°C for higher porosity –90% and impregnation ratio of 2:1 at 500°C.
Yahya et al. [104]	Desiccated coconut residue	Chemical modification with NaOH impregnation	Adsorption of contaminant not evaluated	Micropore distribution is higher with impregnation ratios around 2:500 to 3:600; 500°C provide higher values of SSA (1,400 $m^2\ g^{-1}$).

*Efficiency of the material not evaluated by the authors.

the process. In this scenario, Naushad et al. [109] show the reuse of its new starch/SnO_2 nanocomposite in four adsorption–desorption cycles of Hg^{2+}, obtaining a loss of only 2.5% in the adsorption capacity, what suggests a good regeneration capability.

In this way, it is possible to use agricultural and agroindustrial residues to produce adsorbents and/or activated carbon and to use the produced carbon to decontaminate contaminated water and wastewater, adding value to these agricultural residues.

Finally, the use of vegetal and residual biomass from distinct agroindustry for the production of adsorbents can be a way for resolving these two important issues of environmental pollution, the correct destination of these wastes (agroindustry biomass) and the remediation of environmental compartments containing toxic heavy metals.

3. Conclusion

Although there is a large amount of water in the world, only a part of this water is fresh and suitable for human consumption. Water pollution is one of the most serious environmental problems nowadays, because it pollutes the water sources and leaves it unavailable for consumption.

Anthropogenic activities insert many contaminants into the water resources, inserting toxic metals into the trophic chain. When those amounts reach human beings, these are bioaccumulated and can cause a series of negative effects and health problems. And that is why monitoring and remediate water resources is very important.

Adsorption is a technique widely known and used since antiquity. Although many materials have already been used to produce adsorbents and alternative activated carbons, many other materials still have unexplored potential.

Adsorption process by in natura materials or by activated carbon is a very effective technique to decontaminate water and wastewater containing these toxic metals. These adsorbents can be produced with a large variety of agricultural residues, enabling the production of high capacity adsorbents in any country of the world.

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