Biochar as Alternative Material for Heavy Metal Adsorption

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Biochar is a specific carbon obtained by a pyrolysis process from different feedstocks, as an alternative material for heavy metal adsorption from groundwater. Many studies have been conducted regarding the application of innovative materials to water decontamination to develop a more sustainable approach to remediation processes.

Keywords: adsorption ; biochar ; heavy metals

1. Introduction

Activated carbon (AC) is one of the most used adsorbents for the removal of contaminants in water due to its properties. AC is primarily prepared from coal, coconut shells, lignite, and wood, and activated by physical and chemical methods. Due to its high specific surface area, chemical stability, durability, high capacity of adsorption, and not selective adsorption capacity, AC has been widely used to remove heavy metals from groundwater [1][2][3]. However, the regeneration costs of AC may limit its extensive use [4][5]; therefore, it is important to develop low-cost adsorbents with a high adsorption capacity for the removal of pollutants from aqueous systems [6].

Adsorption onto biochar (BC) is generally considered one of the most cost-efficient and effective treatment methods for removing heavy metals in water and soils [7], and it could represent an alternative low-cost and sustainable adsorbent for contaminant removal from water [4][8]. Biochar is a carbon-rich solid material produced by the thermal decomposition of organic material with a limited supply of oxygen (pyrolysis). It can be produced sustainably under controlled conditions and with clean technologies [9].

BC is produced from various types of wastes such as woody biomass, animal manure, waste paper, and sludges [8][10][11]; it is sometimes also considered a solid by-product, which causes problems in its final disposal. The specific properties of biochar, including its large specific surface area, porous structure, enriched surface functional groups, and mineral constituents, allow it to have a high adsorption capacity [12]. Moreover, BC is easier to prepare and less expensive than active AC or other adsorbing materials [13]. Biochar has a similar porous structure to activated carbon, which is the most widely used and efficient sorbent in the world for removing various pollutants from water. Compared to activated carbon, biochar appears to be a new potential low-cost and effective adsorbent because the cost of biochar is six times lower than activated carbon, due to its lower energy requirements and the fact that it can be used without chemicals or physical activations [14].

2. Biochar

Biochar, which has been known since olden times for its beneficial effects on soil, is produced using the thermal treatment of organic residues from different sources conducted under controlled conditions, i.e., without an oxidising agent [15][16][17][18][19]. Moreover, biochar is a type of specific charcoal that can be obtained by the pyrolysis processing of biomasses with a limited supply of oxygen [20][21][22] and with clean technology [9][23]. In fact, the International Biochar Initiative (IBI) defines biochar as a solid material produced by the thermochemical conversion of biomass in an oxygen-limited condition [24].

The specific properties of biochar, including its large specific surface area (S_{BET}), porous structure, enriched surface functional groups, and mineral constituents, enable it to have a high adsorption capacity [12]. The density and size of its pores, which are generated by the volatilisation of organic substances, depends on the feedstock and on the temperature during pyrolysis [25].

The production of biochar is a process that allows for the valorisation of materials that are substantially considered waste. The Food and Agriculture Organization of the United Nations (FAO) reports that one billion tons of food are wasted every year, of which 60% is solid food waste, such as fruit and vegetable scraps, including peels, seeds, and pips, posing a serious disposal problem [12]. To promote a zero-waste strategy, it is important to highlight the importance of biochar in the circular economy [26]. The transformation of waste into value-added products is one of the alternative solutions to minimise the problem of waste production [27]. In fact, the use of biochar as an environmental application can lead to a reduction in agricultural waste [28] and plant biomass used in the pyrolysis process [29].

Biochar is not only an effective material for environmental remediation but can also be used in other fields [30][31]. In environmental management, biochar can be used for several purposes, as shown in **Figure 1**, including the following: the improvement of soil quality [32][33], greenhouse emission reduction (mainly CO_2), climate change mitigation [34][35], waste and heavy metals management [36][37][38][39][40][41], and as adsorbent material for the removal of heavy metals from contaminated water [42][43][44][45][46].

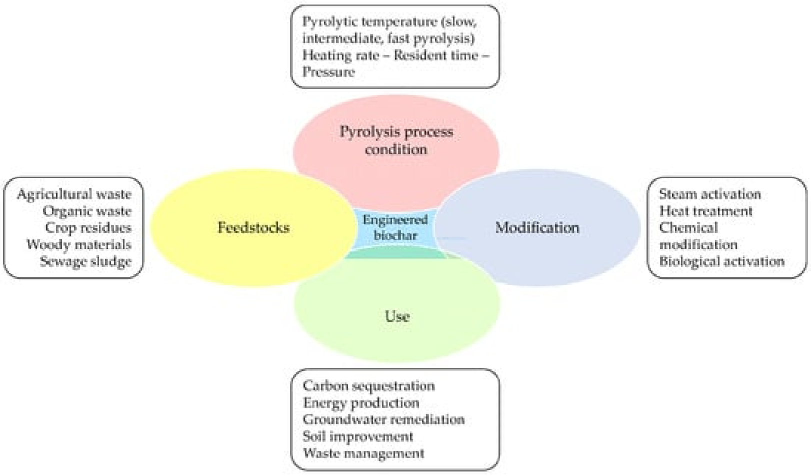

Figure 1. Biochar: origin, preparation, modification, and use.

3. Heavy Metals

Heavy metals are defined as a group of metals and metalloids with a higher density than water [47][48] and a toxic or poisonous effect on humans or the environment at low concentrations [49]. Heavy metals include metals with a density at least five times greater than that of water (i.e., about 5.0 g/cm^3), and some metalloids, such as arsenic [50].

The presence of heavy metal contamination in groundwater is well known due also to natural phenomena such as the erosion and weathering of parent rocks [51]. Natural events such as volcanic eruptions, soil erosion, the rock cycle, atmospheric influences, and tides contribute to the natural cycle of metals, so they reach several environmental compartments, including water, soil, and air [52]. At the same time, groundwater is often contaminated with heavy metals from anthropogenic sources like landfill leachate, sewage, excavation activities, and the uncontrolled disposal of industrial waste [53][54].

The toxicity, mobility, and reactivity of heavy metals depend on their oxidative states, which are influenced by pH, Eh, and temperature [53][55]. Several previous studies reported that the interaction of heavy metals with microorganisms reduced the expression of several enzymes [56][57][58][59]. Furthermore, some heavy metals, at high concentrations, become toxic because they interact with metal-sensitive enzymes, causing the death of some organisms [48].

4. Applications of Adsorption Process for Heavy Metal Removal

4.1. Adsorption Process

The treatment of groundwater contaminated by heavy metals is considered an international challenge [60][61][62][63][64][65]. To restore groundwater contaminated by heavy metals, several remediation technologies have been developed, such as chemical precipitations [66], ion exchange [67], electrokinetic technology, redox methods [68], membrane technologies [69], and permeable reactive barriers [70]; however, the use of these technologies has several contraindications [2][71][72][73]. Therefore, interest in environmentally friendly and economically acceptable treatment technologies for sustainable groundwater remediation [74][75] is growing.

Adsorption is a widely applied technique for removing heavy metals from groundwater [76]. Today, several new adsorbents, such as activated carbon [77], nanotubes [78][79], multi-material nanoparticles, and biochar are being studied as potential sorbents [80][81][82][83]. Adsorption is a chemical–physical phenomenon consisting of the accumulation of one or more fluid substances (liquid or gaseous) on the surface of a solid condensate. In the phenomenon of adsorption, a chemical–physical interaction occurs between chemical species (molecules, atoms, or ions) on the interface between two distinct phases.

The species subjected to adsorption is called the adsorbate, and the solid phase is called the adsorbent [84]. From a thermodynamic point of view, it can be stated that adsorption is a spontaneous process ($\Delta G < 0$) and is characterised by a decrease in the entropy of the adsorbed substance incorporated into the solid ($\Delta S < 0$). Adsorption is an exothermic phenomenon ($\Delta H < 0$) and is therefore favoured by low-temperature values; the amount of heat generated by the process is a function of the type of bonds formed [85]. Depending on the nature of the interactions that occur between the adsorbate and the adsorbent, and thus on the extent of the energy of the bonds with which the particles are retained on the surface, adsorption can be defined as physical, also called physisorption, or chemisorption [86].

Physical adsorption is characterised by weak intermolecular bonds, such as electrostatic or van der Waals, due to the polarity of the adsorbed molecules and the presence of positive or negative ions on the adsorbent surface [87]. Chemical adsorption is, on the other hand, characterised by strong intramolecular bonds, a specific phenomenon that occurs at active sites capable of forming bonds with the molecules of the liquid [88].

The specific behaviour of both processes and the eventual modification in electron density are presented in [86][89][90][91][92].

Adsorption is a superficial process [93]. For this reason, adsorbent materials must have a high specific surface area, which refers not only to the size of the granules of which they are composed but also, and more importantly, to the internal porosity (p) of those granules [94]. The series of treatments by which adsorbents are prepared results in the formation of pores of different sizes [95].

4.2. Column Systems

Studies on adsorption processes at the lab scale can be carried out with two different types of reactors: batch (i.e., discontinuous mode) or column (i.e., continuous flow) [96]. Column systems with continuous flow, as shown in **Figure 2**, are generally used for this kind of experiment. The flow can be upflow or downflow and typically governed by pump systems.

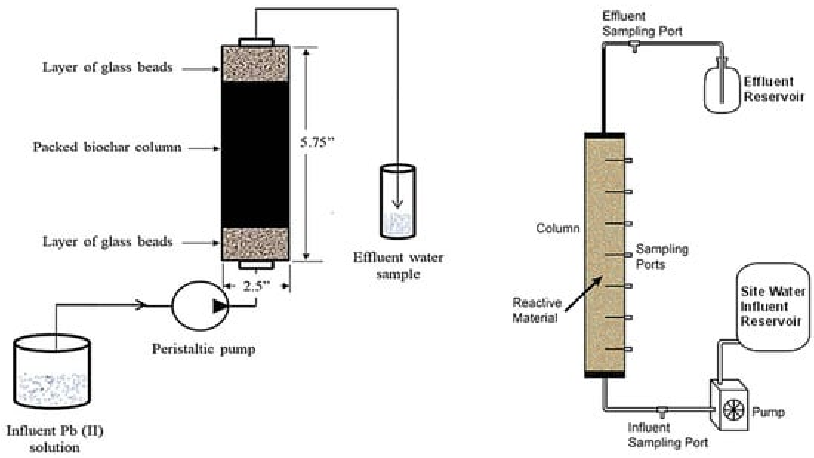

Figure 2. Schemes of possible fixed-bed adsorption systems [97][98][99].

Flow conditions within the column are described by two hypotheses: complete mixing in the transverse direction and the lack of mixing in the longitudinal direction (laminar flow conditions) [100][101]. In both cases, the hydraulic residence time of the liquid in the device is chosen to achieve conditions sufficiently close to thermodynamic equilibrium [102], and steady-state conditions are also generally assumed.

Therefore, in continuous flow processes the adsorbent solid may be arranged as a fixed bed or as a moving bed in contact with the liquid, while the liquid flow may be descending or ascending [103][104][105][106]. **Figure 3** below presents different configurations of the experimental apparatuses used for heavy metal removal through fixed-bed columns and biochar.

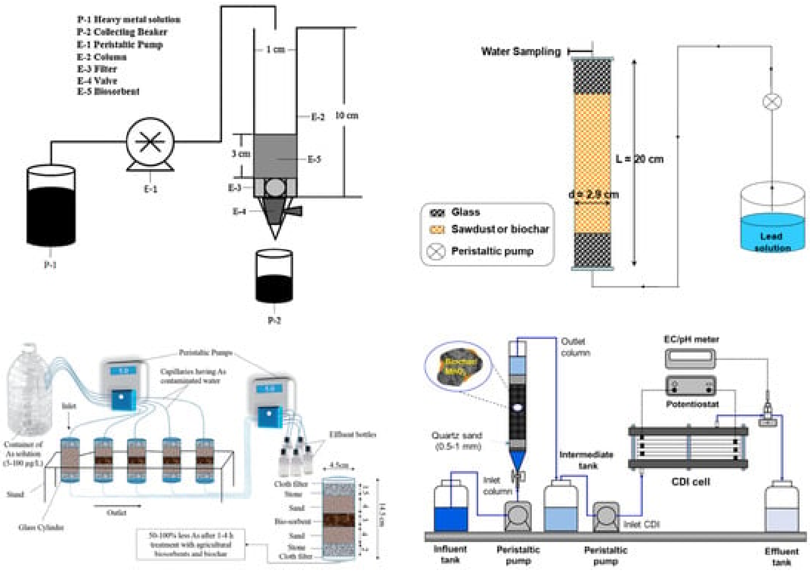

Figure 3. Examples of experimental setups in different studies [107][108][109][110].

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