Aerogels for the Removal of Heavy Metal Ions

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Aerogel is a general term referring to novel nanostructured materials characterized by very high porosity and tunable physicochemical properties that are obtained following a sol–gel process and an appropriate drying method. Such novel materials are entering the market in everyday products and a wide portfolio of properties usable for applications in health care, foods, agriculture, energy, and environmental remediation. Bio-based aerogels obtained from renewable resources and biomass are biodegradable and biocompatible due to the natural origin of the polymers, and for this reason, they greatly contribute to the sustainable concept of the bio-economy, offering promising commodities for environmental remediation.

Keywords: aerogels ; bio-based ; heavy metals ; environmental remediation ; cellulose ; chitosan

1. Introduction

Exponential urban and industrial growth has led to significant impacts on global environmental contamination and on the health of humans and all living organisms [1][2][3][4]. Environmental pollution is one of the most serious issues that need to be addressed to heal the environment, considering the cascading negative effects on air, water, and soil. Among them, water pollution is the sum of effects originating from industrial effluent and waste, municipal effluent, clinical waste, hazardous chemicals, waste from pharmaceutical and personal care products, pesticides, oils, detergents, and so on [5][6]. To solve these pressing issues, novel technologies for wastewater remediation have been developed to reduce, contain, and prevent these phenomena. Adsorption technology has been efficiently designed toward this end over the last few decades, and excellent novel adsorbent materials have been proposed to contain environmental deterioration specifically derived from heavy metal ions and oils [7][8][9][10]. The most widely used adsorbent material is activated carbon, but its use is affected by a series of costs, ranging from production to regeneration [10][11][12]. Furthermore, other adsorbent materials have been evaluated, including zeolites, clays, alumina, silica gels, polymers, and resins [13]. Emerging adsorbent materials that have gained extensive attention for environmental remediation are aerogel-based materials [14][15][16]. Aerogels are a special class of nanostructured materials showing ultra-light weight, high porosity, and tunable physicochemical properties [16][17]. Aerogels can be subdivided into three categories: inorganic, organic, and hybrid. The first category includes silica aerogels; the second includes bio-based aerogels; and the third includes hybrid materials (depending on the composition) [18].

Heavy metal pollution affects environmental health, considering that heavy metals are persistent, non-degradable, and toxic even at very low concentrations. Heavy metals can negatively impact ecosystems by contaminating the soil, the water, and also living organisms due to related bioaccumulation effects [19], making the removal of these ions of prime importance.

The literature reports several methods devoted to the removal of heavy metal ions from wastewater sources using bio-based aerogels as valid alternatives to traditional adsorbents because of their tunable physical–chemical properties, reusability, and simple regeneration processes [20][21].

2. Cellulose-Based Aerogels

Cellulose is a natural polymer widely used for the production of aerogels because of its abundance and the possibility of modifying it by applying several different chemical processes and introducing various functional groups on the surface. Cellulose is generally modified by applying a grafting or crosslinking methodology to improve the chemical and structural stability of the produced aerogels and enrich the material surface with functional groups, such as sulfonate, carboxylate, and phosphonate groups, thus conferring a great affinity for heavy metal ions due to greater electronegative charges on the surface [22][23].

Cellulose-based aerogels modified by introducing an amine group on the surface have several applications for the removal of metal ions. Liu et al. [24] prepared aerogels by functionalizing the cellulose through a crosslinking reaction with the introduction of an amide group able to coordinate Cu(II) ions by physical adsorption and due to a functionalized surface. They found that the Cu(II) adsorption capability derives from a synergy of factors, such as the porous nature of the aerogels, together with the presence of amine and hydroxyl groups. A similar strategy was adopted for the synthesis of nanocellulose functionalized with an amine group [25], which was used for the production of aerogels for the removal of copper from water. SEM images, combined with the spectroscopic ATR-FTIR results, confirmed the role of the amine and hydroxyl groups in ion adsorption.

Aerogels based on cellulose modified with polyethyleneimine (PEI) caught the interest of several scientific groups [26][27][28][29]. Cellulose was functionalized with PEI as a crosslinker, thus allowing the introduction of a great number of amine functional groups on the surface of the cellulose, resulting in aerogels with improved chromium adsorption capability compared to native cellulose and other common adsorbents, such as activated carbon [30] or mesoporous silica modified with amino groups [31]. Two synergistic mechanisms were proposed for the adsorption of chromium: one was based on electrostatic interactions between the protonated amine groups and the chromium ions, while the second mechanism involved the redox reduction of Cr(IV) to Cr(III), balanced by the oxidation reaction of the hydroxyl and amine groups on the material surface [26]. Another paper evaluated the morphological and structural properties of synthetized nanofibrillated cellulose (NCF) after its modification by varying the amount of polyethyleneimine (PEI) [32]. The researchers established the role of PEI in determining the structural stability of the final aerogels, considering that a low amount of PEI corresponds to more fragile materials compared to those obtained with increased PEI content, which were more stable and had a well-defined three-dimensional network. These materials were evaluated for removing Pb(II) from water, and they evidenced a greater adsorption capability with respect to similar adsorbent aerogels.

Aerogels from cellulose nanofibrils (CNFs)/carboxymethylcellulose (CMC) crosslinked with branched polyethylene amine (BPEI) were proposed by Mo et al. as efficient materials for the adsorption of Cu(II) from wastewater with rapid adsorption kinetics [14]. The proposed mechanism for ion capture was based on a dual effect due to the chelation of Cu(II) and ion exchange with active groups, such as hydroxyls, amines, and carboxyls. These aerogels demonstrated an excellent ability to capture metal ions even after ten sorption–desorption cycles.

Another methodology for modifying cellulose adopted the use of several acids, considering that carboxylic functional groups were found to be able to actively participate in ion capture [33][34][35]. In these works, after modifying cellulose with the introduction of carboxylic groups by adding methacrylic acid (MAA), the resulting aerogels showed interesting properties in the adsorption of several ions, such as Ni(II), Pb(II), Zn(II), and Cd(II). The results evidenced the doubled efficiency of adsorption due to the introduction of carboxylic groups on the modified NFC surface. Moreover, after grafting nanofibrillate cellulose with poly (methacrylic acid-co-maleic acid), the presence of two carboxylic groups on the aerogel surface allowed the chelation of divalent ions, as proven by FTIR spectroscopy. Following this strategy, NFC was crosslinked with polyvinyl alcohol (PVA) and acrylic acid (AA) [36], and the resulting aerogel, namely, CNFs-PVA-AA (CPA), showed a stable three-dimensional structure with a greater number of pores with a smaller size compared to the native material, responsible for the removal of metal ions from solution through coordination and ionic bond interactions. The adsorption of heavy metal ions like Cu(II) and Pb(II) was found to reach 30.0 mg/g and 131.5 mg/g when using the developed aerogels. Interestingly, there was also the possibility of reusing the aerogels for up to five cycles of use, with a maintained capacity of adsorption, which makes them good candidates for the purification of wastewater from heavy metals.

Fully bio-based aerogels (FBAs) were synthesized by combining cellulose filaments (CFs), chitosan (CS), and citric acid (CA), resulting in materials with excellent adsorption capacities for methylene blue and copper [37]. The synthetic strategy was defined as simple and scalable, thus providing aerogels with good mechanical properties due to several combined effects, such as electrostatic interactions involving CS and CFs, as well as hydrogen bonding. FBAs were finally characterized to demonstrate that the great availability of several functional groups on the aerogel surface was responsible for the excellent adsorption capacity for heavy metal ions.

Aerogels with the ability to rapidly adsorb ions, such as Cu(II), Cd(II), and Pb(II), were obtained by preparing a composite material from a cellulose nanofiber and chitosan system (CNF/CS) combined with montmorillonite activated by acid [38]. In this work, aerogels were obtained by applying a directional freezing methodology to allow an oriented porous structure, resulting in improved mechanical properties, rapid ion adsorption, and optimal reusability. Aerogels from CNFs were also modified with tannic acid (TA) based on the ability of TA to entrap heavy metal ions by chelating them [39]. These materials were able to adsorb methylene blue, a cationic dye widely used as a colorant in the textile, leather, and paper sectors. Another study proposed an eco-friendly and cost-effective synthesis of cellulose nanofibers (CNFs) grafted with cardanolderived siloxane able to capture Cu(II) ions with an adsorption capacity of 45.6 mg/L, which was higher than those of other bio-based adsorbents [40]. In this research, the role of TA in strongly coordinating metallic ions was established to be associated with the great number of active sites on the aerogel surface due to the multi-phenolic hydroxyl groups participating in the chelation process. Moreover, the developed aerogels manifested a structure characterized by low density that makes them efficient for Cu(II) adsorption.

Aerogels from grafted nanocrystals of cellulose and acrylic acid (AA) were developed and applied for the removal of metal ions, such as Cu(II), Cd(II), and Pb(II) [41]. The highest adsorption capacities of the synthesized aerogels were found to be 872.4, 898.8, and 1026 mg/g for Cu(II), Cd(II), and Pb(II), respectively. The mechanism proposed by the researchers for the adsorption of metal ions was dominated by chemisorption and by the consistency between groups of ion adsorbents, with negative charges from sulfate half-esters, carboxylic groups from AA, and hydroxyl and amine groups acting as binding sites for the metal ions.

Cellulose nanocrystals (CNCs), due to the exposed active groups on the material surface, are susceptible to modification for the production of novel binding sites, thus improving the capability of adsorbing heavy metal ions [42]. CNCs from bamboo pulp were used by Geng et al. for the production of aerogels for heavy metal ion capture. Aerogels were prepared from CNFs oxidized with TEMPO and successively modified with 3-mercaptopropyltrimethoxysilane (MPTs) to give (TO–NFC–Si–SH) as high-porosity aerogels [43]. After their modification, the aerogels showed a great number of thiol groups on the surface that were able to remove Hg(II) ions from water in a wide interval of pH values, with an adsorption capacity of 718.5 mg/g.

Aerogels designed as composites of cellulose and metal–organic frameworks (MOFs) were recently investigated for the capture of heavy metals from solutions. These materials showed excellent adsorption properties correlated with a synergic effect from their very good chemical stability and their large number of functional groups [44]. Metal–organic framework@cellulose aerogel composites were developed by Lei et al. by applying an in situ growth methodology for the production of materials able to capture Cu(II) and Pb(II) ions. The optimal performance reached was 89.40 mg/g for Pb(II); moreover, the materials were recycled for up to five cycles by cleaning with water and mostly maintained their original performance [45]. Also, for these materials, the ion adsorption process was correlated with a mechanism based on the chelation of metal ions with the functional groups on the aerogel.

In another work, hybrid cellulose-based aerogels and metal–organic frameworks were prepared by combining them with a zeolitic imidazolate framework, thus producing aerogels named ZIF-8@CA [46] with high binding potential and a high specific surface area. These hybrid aerogels showed good adsorption capacity for Cr(VI), not only from the surface of the water solution but also from the bottom, with more than 91% removal of the ions; moreover, they evidenced high hydrophobicity and a homogeneous porous structure, overcoming the previous weak properties limiting the final applications. These aerogels were able to reduce Cr(VI) ions in the water and capture heavy metal ions due to coordination with amine ($-NH_2$) and carboxylic active groups (-COOH).

Carbon-based aerogels (CAs) are a class of three-dimensional porous materials with good chemical stability and excellent physicochemical properties that, together with a high surface area, superelasticity, and high-temperature resistance, enable the recyclability of the aerogels [47]. CAs have found applications for environmental remediation in removing heavy metal ions, pollutants, oils, and hazardous solvents [47][48], and recently, bio-based CAs enriched the category with the introduction of CAs developed from bio-masses based on cellulose, lignin, chitosan, and tannin or bio-masses from wastes [10].

Sodium alginate–streptomycin sulfate composite aerogel (Alg–Stre), obtained by chemical grafting, was used for the removal of heavy metal ions, such as Pb(II) and Cu(II), from water [49]. The highest observed adsorption capacities of Alg–Stre for Pb(II) and Cu(II) were considered competitive and selective with respect to a similar adsorbent and were 280 mg/g and 160.2 mg/g for Pb(II) or Cu(II), respectively. The produced materials, characterized by high specific surface area and surface energy, contributed to an extremely fast adsorption speed with excellent performance that was only slightly affected by the temperature.

A shapeable sodium alginate aerogel incorporating modified L-cysteine/UiO-67 was prepared by Du et al. and applied for the removal of Cd(II), Cu(II), and Pb(II) from water [50]. These materials were able to remove great amounts of metal ions (such as 661.2 mg/g for Pb(II), 296.2 mg/g for Cd(II), and 326.4 mg/g for Cu(II)) and to rapidly reach the equilibrium of adsorption. Also, in this case, the improved capability to capture ions was found to be due to the involvement of the functional groups in the chelation process and ion exchange with the metal ions.

Polysaccharide-based aerogels obtained from chitosan and thiourea were engineered by a series of freeze–thaw cycles and combined with formaldehyde to promote the occurrence of covalent bonds [51]. These aerogels were ultra-lightweight materials characterized by a high specific surface area and low density, with a very good capability of adsorbing Pb(II) and Ag(I) ions over five sorption–desorption cycles and very good efficiency after recycling. The selectivity of these aerogels in capturing Pb(II) and Ag(I) ions was associated with the ions' interaction with the –NH and –S groups available on the material surface.

An et al. reported the preparation of a hybrid lignocellulose/chitosan aerogel as a probe for heavy metal detection and adsorption [52]. This material was characterized by an adsorbent skeleton, represented by a hybrid aerogel of cellulose nanofibers and chitosan; a probe for detection based on Rhodamine 6 G; and a crosslinking agent, such as polyvinyl alcohol and glutaraldehyde. This composite material demonstrated interesting hydrophilicity and the rapid capture of several metal ions, such as Hg(II), Ag(I), Al(III), Fe(III), and Cu(II), from wastewater. The developed material was found to be very structurally stable over five sorption–desorption cycles and renewable. The main reasons explaining the material adsorption performance were correlated with the synergic effects derived from a low density and high specific surface area.

A low-cost, eco-friendly calcium alginate aerogel (CAA) was prepared for the removal of lead from aqueous solutions. The results of the investigation revealed that the aerogel had high selectivity and adsorption capacity for Pb(II). The CAA was found to be able to absorb 96.4% of Pb(II) from the aqueous solution, and it could be recovered with a simple acid treatment and reused without any loss in performance [53].

A recent work reported the synthesis of hybrid mesoporous aerogels based on silica and gelatin that are able to selectively adsorb Hg(II) from water containing several heavy metals, such as Cd(II), Cu(II), Pb(I), Ag(II), Ni(II), Zn(II), and Ni(II) [54]. By changing the material composition in terms of %wt of gelatin from 4 to 24%, it was possible to increase Hg(II) removal from the water by up to 91%. Gelatin was found to be able to coordinate Hg(II) and to release it after the aerogels were washed with a solution of a complexing agent such as EDTA. Finally, the aerogels were recovered with unmodified adsorption ability for up to five cycles of continuous use.

3. Chitosan-Based Aerogels

In addition to cellulose, chitosan is frequently used as a porous adsorbent material for the removal of heavy metal ions from wastewater. Chitosan is a linear polysaccharide with a structure characterized by a large number of active groups, such as amino and hydroxyl groups, enabling it to be involved in redox reactions, Van der Waals forces, hydrogen bonds, and other effects involved in the capture of metal ions. Due to the presence of active functional groups, chitosan is generally modified to improve the mechanical and chemical properties and has been successfully combined with other materials, depending on the final desired applications [55][56].

For the removal of Cu(II) from wastewater, Fan and co-workers prepared a responsive composite aerogel from chitosan and poly(acrylic acid-2-(dimethylamino)ethyl methacrylate) via physicochemical double crosslinking that was efficient, recyclable, and able to capture Cu(II) ions with an increased adsorption capacity of up to 660% relative to aerogels made from unmodified chitosan [57]. The capability to entrap Cu(II) was attributed to chelation and complexation phenomena. The adsorption capacity of the prepared composite aerogels reached 70% of the initial adsorption capacity even after six cycles.

Usually, chitosan is combined with cellulose to enhance the adsorption properties and strengthen the mechanical properties of the final aerogels. Li et al. [58] developed composite aerogels from chitosan (CS) and nanofibrillated cellulose (NFC) for the adsorption of Pb(II) from water, which showed a maximum adsorption capacity of 252.6 mg/g. Interestingly, the materials take only 5 min to reach 85% of the equilibrium adsorption capacity for Pb(II) [58], and this peculiar characteristic was attributed to the presence of oriented microchannels obtained via a directional freeze-drying approach. Gao et al. prepared an alginate/melamine/chitosan aerogel for the removal of Pb(II) from water solutions, with a maximum adsorption capability of 1331.6 mg/g at pH 5.5 [59]. The aerogels were regenerated while maintaining a good adsorption capability for up to eight sorption–desorption cycles. In this case, the researchers took advantage of the free amino and aromatic nitrogen groups characterizing the melamine molecule and the useful functional groups, such as hydroxyl amino ($-NH_2$), on chitosan to form complexes with metal ions and remove them from water.

Another composite aerogel was prepared from chitosan and hydroxyapatite and used for the absorption of Pb(II) from wastewater, with a capacity of up to 264.42 mg/g, while that of the porous CS material was only 5.67 mg/g. After the adsorption of Pb(II) ions, the material was regenerated via an ion exchange reaction by replacing the heavy metal ions with a high-concentration solution of Ca(II) ions [45].

High-efficient aerogels from cellulose from pineapple leaves and chitosan from shrimp waste were prepared and used for Cr(VI) removal from wastewater [60]. The research explored several freezing methodologies, including refrigeration and isotropic and anisotropic liquid nitrogen, with the aim of investigating the effects on the final structure of the synthesized aerogel-based adsorbents. The adsorption efficiency for Cr(VI) was proven, as well as the aerogel's excellent reusability. The material behavior related to Cr(VI) adsorption strongly depends on the content of chitosan and the pH of the medium and was correlated with the electrostatic attraction between Cr(VI) oxyanions and protonated amine groups. Starting from the same raw materials, Do et al. developed ultra-lightweight composite aerogels from pineapple leaves, as a source of cellulose, functionalized with TEMPO (2,2,6,6-tetramethylpiperidinyloxy), with the introduction of carboxylate groups able to physically interact with the amino groups of chitosan, thus promoting a stable three-dimensional structure without using a crosslinker [61]. The developed composite materials showed high removal efficiencies for dyes.

Chitosan, after its modification, was also combined with polydopamine to produce aerogels (CS-PDA) using glutaraldehyde as a crosslinking agent [62]. CS-PDA exhibited excellent adsorption ability in the removal of Cr(VI) and Pb(II), with maximum adsorption capacities of 374.4 and 441.2 mg/g for Cr(VI) and Pb(II), respectively. No changes in the material performance were observed after eight sorption–desorption cycles, and the results were correlated with the surface functionalization with glutaraldehyde and with the amino and hydroxyl groups on chitosan molecular chains acting as adsorption sites for heavy metal ions. In a study by Najaflou, a cellulose sulfate/chitosan aerogel (CCA) was prepared using chitosan and cellulose sulfate and used for the removal of Pb(II) from contaminated waters. The CCA was regenerated for up to five sorption–desorption cycles with a reduction in Pb(II) removal of only 10% [63].

Recently, a green aerogel obtained from citrus peel (CP), chitosan (CS), and bentonite (BT) was prepared by Nie et al. and was found to be very efficient in the removal of Cu(II) from water solutions [64]. This aerogel, because of the abundance of active binding sites, showed an excellent Cu(II) adsorption yield of 861.58 mg/g, associated with higher selectivity. The proposed method for Cu(II) capture referred to a binding mechanism between the aerogel and metal cations through electrostatic attraction and chemical chelation between Cu(II) and the active groups on the surface of the material. The aerogel was regenerated by elution with 1 M HNO_3, with little decrease in adsorption efficiency (5.3%) after five cycles.

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