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Abstract Treatment of wastewater pollution is a critical issue in the context of growing population and industrialization. Actual treatment methods are expensive and not fully effective and rely on fossil fuel-derived chemicals, thus calling for alternative adsorption methods on natural materials such as hemp. Industrial hemp (*Cannabis sativa* Linn) is a high-yielding annual industrial crop harvested for its fiber from the stem and its oil from the seeds. Hemp is a multi-purpose plant with great potential because of its many uses, such as building materials, textiles, paper, food and beverage, automotive, cosmetics, and medicine. Wastewater treatment is another innovative application. Indeed, the past decade has shown an explosion in the study of hemp-based materials for the biosorption of metal ions from effluents, demonstrating that industrial hemp is one of the most promising materials for environmental applications. Hemp products can be used as biosorbents in granular or felt forms or to prepare non-conventional activated carbons, both used in biosorption-oriented processes. In this chapter, after a brief description of biosorption, the use of different types of hemp-based materials that can be used as pollutant biosorbents is described.

Keywords Hemp · Biosorbents · Non-conventional carbons · Wastewater treatment · Metals

Abbreviations

ATR-FTIR	Attenuated total reflection Fourier-transform infrared
BTCA	1,2,3,4-butanetetracarboxylic acid
CPMAS	Cross-polarization magic angle spinning
EDX	Energy-dispersive X-ray spectroscopy

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FT-IR	Fourier-transform infrared spectroscopy
IEC	Ion-exchange capacity
MALTO	Maltodextrin
NMR	Nuclear magnetic resonance
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1 Introduction

Industrial hemp is a dicotyledonous plant belonging to Rosales order, Cannabaceae family, and *Cannabis* genus (Fournier 1981; Bouloc 2013; Żuk-Gołaszewska and Gołaszewski 2018), referring to the non-psychoactive varieties of *Cannabis sativa* Linn. One of the oldest domesticated harvests known to man, this plant is grown for the fibers from its stalk and the oil from its seeds. Industrial hemp is a crop giving a yearly high yield of about 30–35 tons/hectare depending on varieties used, cultivation practices, climate, and environmental conditions. This is considered a crop of high industrial value for the bio-based economy due to its renewable and ecological characteristics such as:

- carbon sequestration, suitable for integration in an organic farming system,
- low-cost with easy production, which requires a low level of irrigation,
- no need for pesticides or fertilizers,
- an extremely resistant cultivar,
- unique properties of its products such as fibers and oils,
- sustainable due to the easy local production of an environmental culture adapted to different climatic conditions,
- high yield of natural products provided.

Moreover, hemp is a valuable raw material due to its interesting life cycle analysis (Bouloc 2013; Bono et al. 2015; Crini and Lichtfouse 2020). Hemp cultivation is part of the three pillars of development, and these three components are interdependent (Fig. 1).

Among major crops (*e.g.*, cereals, soybeans), hemp is considered a niche crop. However, its production is currently undergoing a renaissance because this plant is an alternative ecofriendly material that offers many environmental benefits and economic opportunities. Under an increasingly alarming environmental context driven by climate change, biodiversity loss, water pollution, and the need to preserve our planet, among other factors, hemp cultivation is an emerging relevant solution: (i) for agriculture, considering the need for healthy, safe and sustainable production; (ii) for ecology to promote environmentally friendly crops, and to conserve soil and water resources; and (iii) for society as a means for consumers to move towards quality organic products. From an industrial perspective, many fossil-based

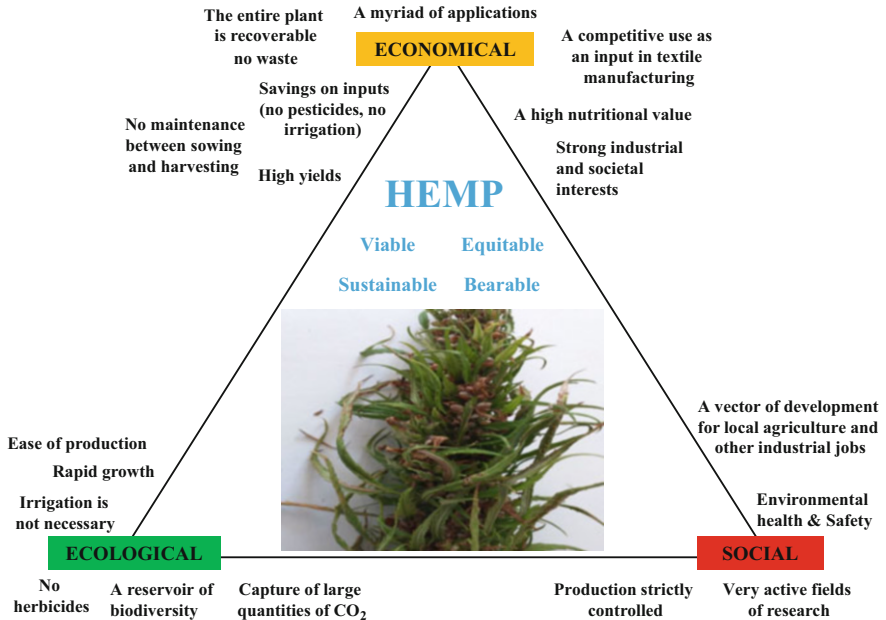


Fig. 1 Hemp and the three pillars of sustainable development: ecological, social, and economical. Copyright G. Crini

materials and applications can be replaced by hemp-based products (Kostić et al. 2003; Bouloc 2013; Ingrao et al. 2015; Cherney and Small 2016; Fike 2016; Crini and Lichtfouse 2020).

China is the largest producer and exporter of hemp. Other important actors in the global hemp market include North America, Korea, Russia, and Europe, where France is the leading producer with a cultivation area of about 17,000 ha, compared to the 170,000 ha cultivated in the nineteenth century. Six products can be recovered from hemp cultivation: seeds, fibers, shives, flowers, dust, and roots. Nowadays, hemp for industrial use is mainly cultivated for its straw from which fiber is extracted (the main product derived from hemp straw) and for its seeds (15–20% of the bulk hemp biomass) which are used to manufacture oil (Crini and Lichtfouse 2020).

From a chemical perspective, the main components of hemp are cellulose, hemicelluloses, and lignin, with minor amounts of other substances, including proteins, pectin, lipids, waxes, and further extractives. Natural lignocellulosic fibers such as hemp, flax, jute, ramie, abaca, kenaf, and bamboo are composed of the three abovementioned main constituents. The minor components are considered as surface impurities. Cellulose, the main biopolymer on Earth, is the main constituent of all plant fibers (about 50–70%), and thus, it influences their characteristics. This polysaccharide is the major structural component of plant cell walls consisting of repeated cellobiose, a disaccharide that has two D-glucose units joined together with β -1,4-glycosidic bond units. After cellulose, hemicellulose is the second major

carbohydrate constituent of lignocelluloses, consisting of carbohydrate monomers. However, hemicelluloses are a mixture of various monomers, composed of short-chain linear and branched heterogeneous structures, typically made of sugars such as xylose, arabinose, galactose, and mannose. The third important substance in lignocellulosic fibers is lignin, the second most abundant component of plant residues. Lignin acts as a cementing material and fills the spaces between the cellulose and the hemicelluloses, the three components bonded together by covalent bonds. From a more general perspective, lignin is one of the most abundant organic compounds on Earth, along with cellulose, starch, and chitin. It is a complex bio-polyol containing aromatic moieties with a high molecular weight and a complex amorphous and irregular structure, which is still unknown and represented by hypothetical formulas.

The technical fibers, obtained by processing hemp stalks, are composed of elementary fibers bonded together into bundles by the middle lamella, mainly comprised of pectin encrusted with lignin (Placet et al. 2014). In contrast, the elementary fibers consist of several cell walls formed from oriented semi-crystalline cellulose microfibrils embedded in a hemicellulose-lignin matrix. Hemp as lignocellulosic material has a high cellulose content with low lignin and hemicellulose amounts, which is why this feedstock is used in fiber production, *i.e.*, higher cellulose content correlates with high strength and stiffness, being also ideal for polymer reinforcement. The chemical composition is also heterogeneous but less than other lignocellulosic biomasses. This is of great importance, for example, in fermentations of lignocellulose-derived sugar streams for applications in biorefineries.

There are two types of fibers (Placet et al. 2014): long bast fibers representing 20–25% of the bulk hemp biomass, and woody short core fibers in granular form from shives or hurds, representing 45–50%. As a member of the bast fiber family, hemp contains over 75% cellulose and less than 10–12% of lignin compared to the content in the wood of 60% and 30%, respectively. The bast fibers contain higher amounts of cellulose than the shives. Given their different physical properties, the two types of fibers have different ideal end uses. Hemp dust is a by-product of hemp processing, accounting for 15–20% of bulk straw. In recent years, it has been seen as a potential revenue-generating material for the future challenge of renewable energy production, *e.g.*, usable in the methanization process. This challenge could be a relevant solution for waste management in the hemp sector and renewable energy production on a local scale. After fiber recovery, shives or hurds from hemp straw have minor applications for animal bedding, garden mulch, and lightweight concrete but are now considered a high value-added product as feedstock for biorefinery. Similarly, once considered industrial wastes, the flowers and roots are the subjects of numerous studies, especially in medical research. However, these products have not yet been considered as potentially revenue-generating material.

For millennia, hemp has been a source of fiber, protein, and oilseed used worldwide to produce a variety of human consumption products for food, shelter, clothing, and heat. Crini et al. (2020) recently reviewed and discussed the traditional and new applications of hemp. In fact, hemp and its products have found applications in numerous sectors (Fig. 2) such as pulp and paper, textiles, construction, food

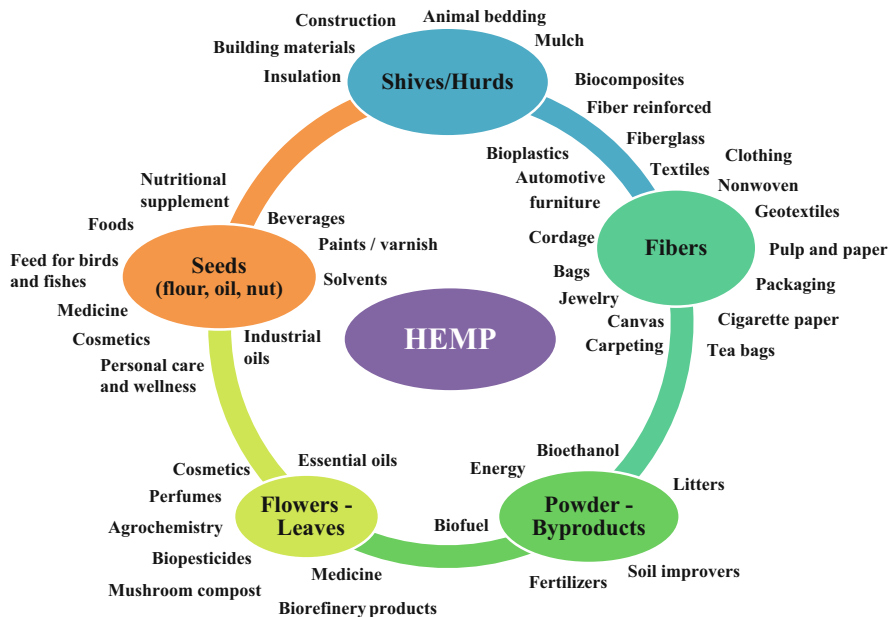


Fig. 2 The main applications of the five products recovered from a hemp plant, fibers, shives and seeds being the most important ones. Copyright G. Crini

and beverages (beer and wine industries), animal nutrition, horticulture, automotive industry, and the following composites: bioplastics, packaging, composites for airplanes and furniture. Hemp fiber is used to produce apparel, fabrics, papers, cordages, and building materials for insulation, panels, and roofs. The shives or hurds, long considered as a waste byproduct of fiber production, are used for bedding of animals, *e.g.*, mulch for horses and kitty litter, or energy production, the seeds for human nutrition, *e.g.*, as flour, and the oil for a wide range of purposes, from cooking to cosmetics. Other sectors under development are cosmetics and essential oils, jewelry and fashion, nutraceuticals, pharmacy, medicine, *e.g.*, traditional Chinese medicine, agrochemistry, adhesives, biotechnology, biofuel, and energy production phytoremediation. Other innovative applications such as paints, printing inks, detergents, solvents, nanotechnology, bioprinting, solar panels, bioactive substances, and bio-pesticides open new challenges. More than 25,000 products are made from or contain hemp (Rehman et al. 2013; Bono et al. 2015; Dunford 2015; Cherney and Small 2016; Fike 2016; Ummartyotin and Pechyen 2016; Bran et al. 2017; Bonini et al. 2018; Chalupa-Krebzdak et al. 2018). In recent years, potential applications in soil phytoremediation and wastewater treatment have also been proposed (Crini and Lichtfouse 2020; Crini et al. 2020; Tofan et al. 2020).

After a brief description of biosorption, this chapter describes the potential use of hemp-based materials, in the form of biosorbent or activated carbon, in wastewater treatment for pollutant removal. For this, an extensive list of publications has been compiled and discussed, and examples from our work are also presented.

2 Biosorption of Pollutants Present in Wastewaters

2.1 Water Pollution by Metals

Whether domestic, agricultural, or industrial, all activities produce effluents containing undesirable, even toxic, pollutants, among which metals are often cited. Indeed, among the various industrial activities, the surface treatment industry widespread across Europe is considered one of the largest water and chemical consumers and polluters (Morin-Crini and Crini 2017). This industrial sector is characterized by small structures (usually less than 100 people), closely linked to the automotive, mechanical, and aeronautical industries. The household appliance, telecommunications, nuclear, and space markets are also growth drivers. Despite a gloomy industrial context, the surface treatment industry is dynamic and constantly evolving. However, this industrial activity still has a bad image in terms of water pollution. Although considerable efforts have been made by the industrial sector over the last 30 years, water pollution remains a major concern.

Industrialists use a lot of water and chemicals in their processes, thus producing large quantities of polluted water. These wastewaters are acknowledged as being among the most contaminated of all industrial effluents. They contain a range of inorganic (metals, salts, anions) and organic pollutants, some of which can react with each other (Druart et al. 2016; Euvrard et al. 2014). Before being discharged into the environment or an urban wastewater treatment plant, industrial effluents are treated in order to comply with emission limit values set by regulations. However, the discharged waters still contain remarkable amounts of pollutants. Among them, metals (most often Cu, Zn, Ni, Sn, and Cr) are commonly found at concentrations in the mg/L range, and organic molecules, such as polycyclic aromatic hydrocarbons, volatile organic compounds (chloroform), and alkylphenols, can occur at concentrations varying from hundreds of ng/L to some µg/L. The discharge of metals into the environment is a serious environmental problem affecting water and soil quality, directly endangering human health (Priac et al. 2014). They can have a toxic or inhibitory effect on living organisms, and their release in aquatic ecosystems worries society and governments. In this sense, many metals have been classified as high-priority (*e.g.*, Cd, Hg, Pb) or priority (*e.g.*, As, Cr, Ni, Cu, Zn) hazardous substances (Morin-Crini and Crini 2017).

On an industrial scale, the technologies that can be used to remove metals are chemical precipitation assisted with a coagulation/flocculation step and/or an oxidation step, electrocoagulation, cementation, membrane filtration (reverse osmosis), adsorption on activated carbons, ion-exchange on chelating resins, liquid-liquid extraction, and evaporation (Zhao et al. 2016; Morin-Crini and Crini 2017; Crini and Lichtfouse 2019a; Kaushik and Singh 2020; Vidu et al. 2020). Each technology has its constraints in terms of cost, feasibility, efficiency, practicality, environmental impact, sludge production, operation difficulty, pre-treatment requirements, and the formation of potentially toxic byproducts. In general, precipitation is the method chosen by the industry for reasons of efficiency, technical ease, and especially

economics. However, like the other methods mentioned, this treatment technology is ineffective for treating low concentration effluents. For example, because of their high cost and problems of rapid saturation, adsorption onto commercial activated carbons is employed more frequently to remove organic compounds rather than metals. Polymeric resins show excellent complexation abilities, reaching ppb levels in removing metals, but their widespread use is restricted due to the high cost. In addition, ion-exchange is very sensitive to the pH of the solution and the organic load present in effluents, two important issues in the surface treatment industry. It is then necessary to protect the resins by an upstream step (*e.g.*, activated carbon), which increases the financial costs. Membrane filtration is also known as a potential technology to treat dilute effluents. However, small and medium-sized enterprises are not enthusiastic about the idea of investing in such additional treatment due to the high initial investment needed and its complicated maintenance.

Thus, there is an interest in developing new removal strategies that are simple, low-cost, effective, eco-friendly, and especially acceptable for industrial use. Amongst the latest techniques for pollutant removal proposed as secondary or tertiary (final) steps in a treatment plant, liquid-solid biosorption-oriented processes are a procedure of choice to remove metals present in diluted effluents.

2.2 Biosorption Technology

Liquid-solid biosorption is defined as removing metals from solution by inexpensive biological materials called biosorbents (Gadd 2009). Biosorption is a property of both living and dead organisms and their components, which has received significant attention in the last three decades as an alternative process for the recovery of toxic or precious metals present in aqueous solutions (Gavrilescu 2004; Gadd 2009; Park et al. 2010a; Mudhoo et al. 2012; Michalak et al. 2013; Fomina and Gadd 2014; Gorska et al. 2014; Kyzas and Kostoglou 2014; Gupta et al. 2015; Vijayaraghavan and Balasubramanian 2015; De Gisi et al. 2016; Okenicova et al. 2016; Krstic et al. 2018; Singh et al. 2018; Crini et al. 2019; Escudero et al. 2019; Kapahi and Sachdeva 2019; Lindholm-Lehto 2019; Varghese et al. 2019; Beni and Esmaeili 2020; Calderon et al. 2020; de Freitas et al. 2019; Ghomi et al. 2020; Musarurwa and Tavengwa 2020; Na et al. 2020; Qin et al. 2020; Singh et al. 2020; Tamjidi and Ameri 2020).

In a biosorption-oriented process, the separation is based on a simple mass transfer from the liquid phase to the solid phase, similar to those encountered in the classical adsorption process using commercial products such as activated carbons. However, the interactions and the adsorption mechanisms are different. Biosorption is a result of passive binding through several physical and chemical mechanisms, including van der Waals forces, hydrogen bond, electrostatic interactions involving charged species, ionic and covalent bonds. In general, the affinity between the biosorbent and the pollutant is the main driving force controlling the process (Crini and Badot 2010; Crini and Lichtfouse 2019b).

Table 1 Principal requirements to be taken into account for choosing a biosorbent material to remove pollutants from aqueous solutions (Crini 2005, 2006; Crini and Badot 2010; Crini and Lichtfouse 2019b)

Low cost and readily available
A well-developed structure
Porous material with a large total surface area
Surface charge (acidity/basicity properties)
Presence of adsorption sites or functional groups
Versatile materials with different forms (granular, etc.) and good particle size distribution
Appropriate mechanical properties and high chemical stability (not disintegrating in solution)
Efficient for removal of a large range of pollutants
High capacity, selectivity, and rate of adsorption
A long life
Capable of regeneration if required
Capable of being incinerated to recover pollutants (metals)

For many adsorption/biosorption processes, separation is caused by a mass separating agent, called an adsorbent or biosorbent, possessing particular textural, physical, and chemical properties (Dąbrowski 2001). Unlike conventional adsorbents, biosorbents have a biological origin. They are also cheap, abundant, and often widely available, with intrinsic complexing and chelating properties. The performance of any adsorptive separation or purification process is directly related to the quality and properties of the material, including its specific surface area and porosity. Indeed, as adsorption is mainly a surface phenomenon, the highest performances are described with porous materials having large surface areas, which favors exchanges and interactions (Crini 2005). However, an ideal biosorbent must meet several other conditions listed in Table 1. For example, it must have a particle size, shape, and mechanical strength suitable for reactors under continuous flow conditions, such as ion-exchange resins. Metal uptake must also be not only efficient but also rapid and economically feasible.

Crini (2005, 2006) proposed a simplified classification of adsorbent materials by distinguishing two main types: the first category includes conventional (commercial) adsorbents such as activated carbons, ion-exchange resins, and inorganic materials (aluminas, silica gel, zeolites), and the second includes non-conventional adsorbents such as activated carbons obtained from agricultural solid wastes and industrial by-products, natural materials such as clays, industrial by-products (red mud), and biosorbents.

Since the 1990s, a large variety of biosorbents have been proposed and studied for their ability to remove inorganic and organic contaminants. Numerous studies concern metals in particular (Hubbe et al. 2011; Salman et al. 2015; Tran et al. 2015; Vandenbossche et al. 2015; Suba and Rathika 2016; Kumar et al. 2017; Crini and Lichtfouse 2019a, c; Crini et al. 2019). The list of materials includes, for example, dead biomass, peat, agro-food and agricultural wastes, *e.g.*, sawdust and bark, industrial by-products, living plants, fungi, algae, bacteria, biopolymers such

as chitin, chitosan, cellulose, starches, and alginates, or other products, *e.g.*, cyclodextrins. Much attention has also been focused on various hemp-based materials as biosorbents. These materials are competitive with conventional materials, *e.g.*, carbons and resins, or other adsorbents, *e.g.*, zeolites and clays, because they represent abundant and cheap materials that are worldwide available and often have high affinity, capacity, and selectivity. Materials made from hemp also meet most of the conditions described in Table 1 (Salman et al. 2015; Rezić 2013; Balintova et al. 2014).

2.3 Biosorption of Pollutants Using Hemp-Based Products

Liquid-solid adsorption processes that use commercial materials or non-conventional materials, including hemp, are often performed in batch mode, by adding material to a vessel containing the contaminated solution (batch methods) or by feeding the solution continuously through a packed bed of material (fixed-bed reactors, dynamic continuous-flow systems) (McKay 1996). In the literature, batch methods are widely used to describe biosorption capacity and kinetics for several reasons: their operation is simple and inexpensive, the experimental protocols are well-established, the data are reproducible, and the results are easily interpreted. The solution's parameters, *e.g.*, pH, temperature, and ionic strength, can also be controlled and adjusted, providing extensive experimental data that can be easily modeled.

Figure 3 illustrates the forms of hemp-based materials used as biosorbents in a batch experiment. In a classical experiment, a given mass of hemp is mixed with a volume of an aqueous pollutant solution at a known concentration in a contacting reactor, under previously established conditions of stirring rate, stirring time, concentration, pH, ionic strength (if necessary), and temperature. The solution is then stirred for a specified time (t) or for a time to attain equilibrium (t_e). At the end of the experiment, the solid sorbent and sorbate in the solution are separated, and the final concentration of the pollutant in the solution is analyzed. This analysis gives the concentration in the supernatant (C_t at time t or C_e at time t_e), which by comparison with that of the initial solution (C_o) allows the calculation of the efficiency of the



Fig. 3 Different forms of hemp-based materials: (a) powders, (b) shives or hurds, (c) fibers and (d) felt. Copyright G. Crini

hemp material, *i.e.*, its performance in terms of pollutant elimination (McKay and Al Duri 1989; Tien 1994; McKay 1996; Manes 1998; Cooney 1999; Crini and Badot 2010; Crini and Lichtfouse 2019b; Beni and Esmaeili 2020). The amount of pollutant adsorbed (q_e) at equilibrium time (t_e) by the adsorbent is calculated from the mass balance equation given by Eq. (1) where C_o and C_e are the initial and final pollutant concentrations in the liquid phase (mg/L), respectively, V is the volume of pollutant solution (L) and m is the mass of hemp used (g).

The data from the experimental adsorption studies allow the solid phase concentration to be plotted against the liquid phase, depicting an equilibrium adsorption isotherm. This isotherm represents the relationship between the amount of pollutant adsorbed and the pollutant concentration remaining in the solution. Equilibrium is established when the amount of pollutants being adsorbed onto the material equals the amount being desorbed. These curves can be modeled using many theories related to adsorption equilibrium, among which the Langmuir model is the best known. This model is represented by the Eqs. (2) and (3) where x (mass, mg) is the amount of pollutant adsorbed, m (g) is the amount of adsorbent used, C_e (mg/L) is the liquid phase concentration of adsorbate at equilibrium, q_e (mg/g) is the solid phase concentration of adsorbate at equilibrium, and K_L (L/g) and a_L (L/mg) are the Langmuir isotherm constants. These constants are evaluated through the linearization of Eq. (2). Hence by plotting C_e/q_e against C_e , it is possible to obtain the value of K_L from the intercept, which is $1/K_L$, and the value of a_L from the slope, which is a_L/K_L . Although the Langmuir model uses an empirical equation (Hamdaoui and Naffrechoux 2007), it is widely used in the literature because it obtains a parameter, namely the theoretical monolayer capacity (q_{max} in mg/g). Its value is numerically equal to K_L/a_L and corresponds to the maximum adsorption capacity of an adsorbent.

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

$$q_e = \frac{x}{m} = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (3)$$

3 Applications of Hemp-Based Products as Biosorbents

3.1 Hemp as a Novel Material for Metal Removal

As previously mentioned, treatment methods such as ion-exchange or chelation onto organic resins and/or adsorption onto activated carbons are not economically viable

Table 2 Advantages and drawbacks of using hemp-based materials for metal removal by the biosorption-oriented process

Advantages	Disadvantages
<p>Emerging recovery technology, publicly acceptable</p> <p>Economically feasible: a low-cost resource for applications in pollutant removal</p> <p>Raw hemp: a renewable, biodegradable, and environmentally friendly resource; an abundant material and widely available in many countries; a functional and hydrophilic biopolymer (mainly cellulose) with high reactivity</p> <p>A remarkably high swelling capacity in water</p> <p>A versatile material: biosorbents can be used under different forms (powders, fibers, felts)</p> <p>Materials can be easily modified by different chemical treatments and grafting reactions</p> <p>Technologically simple: simple equipment, adaptable to many treatment formats; can be applied to different flow regimes (batch, continuous)</p> <p>Capable of treating large volumes</p> <p>Outstanding metal-binding capacities</p> <p>Efficient at trace levels</p> <p>Rapid kinetics</p> <p>High selectivity</p> <p>Chemisorption mechanism clearly established: electrostatic attraction, ion-exchange, complex formation</p> <p>After use, materials can be burned and metals recovered (<i>e.g.</i>, for catalysis)</p> <p>Shives as abundant and low-cost byproducts can be used to prepare activated carbons</p>	<p>Technology is still being developed; laboratory stage</p> <p>Materials with a low surface area</p> <p>Variability in the materials used</p> <p>A tendency to shrink and/or swelling</p> <p>Not appropriate for column systems (excepted in felt form)</p> <p>Impact of the solution pH on the biosorption performance</p> <p>Modified materials: results depend on the functional groups grafted</p> <p>Requires chemical pretreatment to remove other pollutants (pesticides)</p> <p>Little effect on the chemical oxygen demand</p>

for treating trace metals present in effluents. Conventional processes, such as chemical precipitation used at an industrial scale, are also not competitive for dilute solutions. On the contrary, an overview of the literature data shows that hemp-based technology is particularly feasible as an alternative for removing metals from dilute and concentrated effluents and waters and for treating large volumes. The recent results published by Romanian group of Păduraru, the Serbian group of Kostić, and the French group of Crini demonstrated that biosorption using non-conventional hemp-based adsorbents is an effective, economical method for metal removal while being technologically simple and easily transferable to industrial scale. Hemp-based materials have an extremely high affinity for many metals commonly used in industry and outstanding biosorption capacities. Morin-Crini et al. (2019) recently published the first comprehensive review on metal sequestration by these materials. Table 2 describes the advantages and disadvantages of using hemp products in biosorption-oriented processes often cited in the literature.

Copper is often present in discharged waters from the metal industry because of its wide use. The regulatory value for this chemical element is 2 mg/L in the discharged waters. It is also included in the list of priority pollutants defined by

Table 3 Adsorption capacities (q_{\max} in mg/g) for copper using hemp-based biosorbents

Hemp-based biosorbent	Conditions: biosorbent dosage; pH; contact time	q_{\max}	Reference
Raw fibers		9.07	Păduraru and Tofan (2002)
Raw fibers		9.5	Demirbas (2008)
Bleached fibers impregnated with α -benzoinoxime		8.03	Tofan and Păduraru (1999)
Fibers impregnated with α -benzoinoxime		13.8	Tofan et al. (2001a)
Shives	1 g/100 mL; 4; 24 h	3.91	Balintova et al. (2014)
Shives treated with NaOH	1 g/100 mL; 4; 24 h	4.45	Balintova et al. (2014)
Shives treated with HCl	0.75 g/75 mL; 5; 24 h	5.48	Rozumová et al. (2018)
Raw shives	1 g/100 mL; 5; 2 h	2.87	Unpublished results
Shives treated with Na_2CO_3	1 g/100 mL; 5; 2 h	10.2	Unpublished results
Modified shives with BTCA ^a	1 g/100 mL; 5; 2 h	10.1	Unpublished results
Raw felt	0.25 g/100 mL; 5; 1 h	14.6	Bugnet et al. (2017b)
Raw felt	0.25 g/100 mL; 5; 1 h	14.6	Loiacono et al. (2017a)
Carboxylated felt	0.25 g/100 mL; 5; 1 h	63.3	Loiacono et al. (2017b)

^a 1,2,3,4-butanetetracarboxylic acid

the French Water Agency (French Circular, July 27, 2015). However, it is a difficult element to eliminate when it is present in diluted polycontaminated discharged waters. For this reason, copper is often studied as a target pollutant in biosorption studies (Morin-Crini et al. 2019; Tofan et al. 2020). For example, Loiacono et al. (2017b) demonstrated that 1 g of hemp-based material could adsorb 63.32 mg of Cu present in an aqueous solution. Table 3 presents maximum adsorption capacities (q_{\max} in mg/g) for Cu removal obtained on different hemp-based materials, mainly under batch studies.

3.2 *Hemp Fibers as Adsorbents*

Păduraru's Romanian research group was the first to propose, at the end of the 1990s, the use of hemp fibers to complex metals (Tofan and Păduraru 1999, 2000; Tofan et al. 2001a, b; Păduraru and Tofan 2002). Their investigations clearly

indicated that hemp fibers, as wastes from the textile industry, were very useful for the treatment of metal-contaminated wastewaters, presenting high adsorption capacity for metal removal. Before use, the fibers were purified by boiling for 4 h in a solution containing soap and soda ash and then washed several times with water and dried in an oven at 45 °C. For more than 10 years, this group has published numerous studies using batch protocols (Tofan and Păduraru 2004; Tofan et al. 2009, 2010a, b, c, 2013, 2015, 2016a, b, 2020; Păduraru and Tofan 2008). The metals present in aqueous monometallic solutions studied included Cd, Co, Cr, Cu, Pb, Ag, and Zn. Biosorption capacities ranged from 7.5 to 13.5 mg of metal eliminated per gram of fiber, depending on the metal and applied experimental conditions. Using spectroscopic data, the authors demonstrated the presence of strong bonding between metals and carboxylic (present in hemicelluloses, pectin, and lignin), phenolic (lignin and extractives), carbonyl (lignin), and hydroxyl (polysaccharides) groups, which allowed to conclude that chemisorption of metals occurred *via* electrostatic interactions, complexation, and ion-exchange.

In a comprehensive study, Păduraru and Tofan (2002) reported that, under all the experimental conditions tested, the order of affinity was the same: $\text{Cu} > \text{Cr} > \text{Cd} > \text{Ag}$. The q_{max} values were 9.07, 4.0, 2.59, and 1.22 mg/g for Cu, Cr, Cd, and Ag, respectively. Other results demonstrated that hemp waste materials efficiently removed Co, Pb, and Zn from diluted and concentrated aqueous solutions. Besides the low effectiveness of these hemp materials, these biosorbents have two main advantages: low cost and non-toxicity. In all cases, chemisorption was the main mechanism to explain the adsorption data.

In another work, Tofan et al. (2010b) evaluated the thermodynamic feasibility of the Pb biosorption process on hemp at different temperatures between 5 and 60 °C. The biosorption isotherms and kinetics showed that the experimental data were better fitted by the Langmuir equation and the pseudo-second-order equation. Isotherms were characterized by a steep increase in the biosorption capacity, indicating a great affinity of the material for the metal, followed by a plateau representing the maximum capacity at saturation of the monolayer. The Langmuir model was also the most appropriate for describing the adsorption process for all the metals investigated. Under the studied temperatures, the Gibbs free energy change (ΔG) values were negative, showing the feasibility and spontaneous nature of Pb biosorption on fibers. The positive values of enthalpy change (ΔH) indicated that Pb biosorption was an endothermic process favored by temperature increase. The positive value of entropy change (ΔS) suggested increased randomness at the interface of hemp-solution and high affinity of the hemp fibers for Pb ions.

Păduraru's group also studied the regeneration of hemp fibers after use, which consisted of an easy, simple, and low-cost immersion in an acidic solution; here, the protons in the solution replaced the metal ions on the loaded hemp. Batch desorption and multiple adsorption-regeneration cycles for Zn removal by hemp fibers were investigated (Tofan et al. 2016a). The efficiency of Zn desorption with 0.1 M HCl was higher than that achieved using an equimolar solution of H_2SO_4 . The adsorptive potential of the tested hemp remained almost unchanged after three cycles of

adsorption-desorption of Zn, showing the chemical stability of the biosorbents and the repeatability of the results simultaneously.

Physical or chemical modification of raw fibers can improve their removal performance and selectivity for metal cations and thermal properties. For example, the grafting of various functional groups onto fibers can increase the density of biosorption sites and modify the diffusion properties of the biosorbents. However, this chemical treatment can directly alter natural fibers' surface and bulk chemical compositions and remove significant amounts of components such as cellulose and hemicelluloses. Therefore, it is important to characterize the modified fibers. Chemical treatment has been proposed using (γ -mercaptopropionic acid as a chelating agent to introduce sulfhydryl functional groups onto fibers' surface (Tofan and Păduraru 2004). For raw and modified hemp, under similar experimental batch conditions, the adsorption capacities were 1.22 and 10.75 mg/g for Ag and 2.59 and 14.05 for Cd, respectively. The data demonstrated the important role of sulfhydryl chelating groups.

Tofan et al. (2013, 2015) also investigated the interaction between hemp and metal ions using fixed-bed column studies. For Co removal, the biosorption capacity of the fibers used in the column ($q_{\max} = 15.44$ mg/g) performed slightly better than that of the batch system ($q_{\max} = 13.58$ mg/g). These results were explained by decreasing the gradient concentration with time in batch experiments while the gradient continuously increased in the interface of the biosorption zone in the column (Tofan et al. 2013). Significant results were also obtained for Cr removal from aqueous solutions by adsorption in a fixed bed column filled with alizarin S impregnated hemp fibers (Tofan et al. 2015). However, practical industrial applications of hemp fibers in column-based biosorption processes are limited due to hydrodynamic limitations. A more adaptable solution would be using the materials in the form of felts in filtration-adsorption processes. From their numerous results obtained in batch and column experiments, Păduraru's research group concluded that hemp-based materials might be useful as biosorbents in wastewater treatment and a promising alternative to replace conventional materials used for metal removal (Tofan et al. 2020).

In a series of works, Kostić's group also focused on the interaction between metals and short hemp fibers as waste material from the textile industry (Pejić et al. 2008, 2009, 2011; Kostić et al. 2007, 2008, 2010, 2014; Milanovic et al. 2012; Vukčević et al. 2014a, b). Their results demonstrated the ability of hemp to act as an effective biosorbent for the removal of metals (Cd, Zn, Pb) from both single and ternary aqueous solutions. The order of the affinity was $\text{Pb} > \text{Cd} > \text{Zn}$ (conditions used in the batch: 0.5 g of fiber in 200 mL metal solution, contact time 2 h), in agreement with the results published by Păduraru's group. Kostić's group used both raw fibers and fibers modified by simple and inexpensive alkaline (NaOH at room temperature) and oxidative (NaClO_2 at pH = 4 and boiling temperature) treatments, aiming to study the influence of fiber chemical composition on their metal adsorption potential, to increase the adsorption capacities of the raw adsorbent materials, and to establish a relationship between the chemical composition of hemp fibers and their uptake capacities for metals (Pejić et al. 2009). In that study, the treatments used to

modify the materials originated with different adsorption properties. Regardless of the target metal, the modification with sodium chlorite resulted in superior performance compared to alkali modification. To explain this result, the fibers before and after chemical treatment were characterized by chemical, physical, microscopic, and spectroscopic techniques. The chemical composition of raw and modified fibers was determined, demonstrating that alkaline treatment removed hemicelluloses (approximately 70% concerning raw fibers). However, lignin was resistant to chemical degradation, while treatment with sodium chlorite removed lignin by about 50% and hemicelluloses by ca. 17%. Moreover, modification with sodium chlorite resulted in the formation of carboxylic groups at the surface of the fibers, which favored adsorption properties.

The accessibility of the cell wall components to aqueous solutions was evaluated by determining the degree of fiber swelling and water retention value. The data analysis showed that treatments caused gradual removal of hemicelluloses or lignin, modified the fiber surface, and altered its structure. For example, hemicellulose removal increased the degree of fiber swelling and decreased the water retention value of hemp fibers, while lignin removal decreased the degree of fiber swelling and increased the water retention of fibers. The chemical treatments have also affected the amount and accessibility of functional groups incorporated in the fiber structure. A relationship between the textural characteristics of biosorbents and their adsorption properties was highlighted. An observed increase in adsorption properties was ascribed to the decrease in lignin or hemicellulose content and the increased fiber fibrillation, surface peeling, and roughness, affecting the fiber-specific surface area.

Another important conclusion on the role of active sites has been demonstrated. The removal of substances present on the surface of the fibers by both chemical treatments leads to the release of functional groups and an increase in their quantity. Since functional groups act as active sites for adsorption, chemical modification efficiently improves the adsorption properties of biosorbents. Therefore, the different performances of the materials were explained by significant changes in the surface and structure of the fibers and differences in the surface properties of the fibers (quantity and accessibility of active sites). A mathematical model based on the determination of diffusion coefficient and the concentration profile of metal ions through the fiber has been used to describe the adsorption mechanism and optimize the process. This model provided a better insight into phenomena of cations transport through porous fiber matrices and permitted to optimize the metal biosorption by connecting the model parameters with the fiber performances (Pejić et al. 2011).

Kostić's group concluded that short hemp fibers could be used as low-cost adsorbents to remove metals present in mono- or polycontaminated solutions, and the mechanism was mainly driven by chemisorption (ion-exchange on acidic functional groups). The fibers could be useful for designing batch or continuous biosorption processes to treat industrial effluents (Vukčević et al. 2014a). The authors pointed out that the accessibility of the cell wall components to aqueous solutions played an important role in the performance of hemp fibers for metal removal and the surface reactivity of the fibers.

Kyzas et al. (2015) demonstrated that raw fibers presented high biosorption capacities toward Ni, between 160 and 206 mg of Ni per gram of material, regardless of its concentration. The adsorption mechanism was chemisorption rather than physisorption, and the differences in the degree of performance were mainly attributed to the hemp form used (fibers or granular). In the same report, the fibers modified with NaOH or citric acid showed improved capacities, namely 237 mg/g when treated with NaOH and 242 mg/g when treated with citric acid. A detailed characterization study using data from Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy images (SEM), elemental analysis using energy-dispersive X-ray spectroscopy (EDX), crystallinity, and cellulose content showed that textural changes in the surface of fibers could explain this increase in performance. Kyzas et al. (2015) also indicated that the raw and modified materials could be easily regenerated and were reusable for more than ten cycles. The biosorption capacities remained unchanged after regeneration, showing the chemical stability of the modified materials and the reproducibility of the biosorption process. The authors also reported that Ni uptakes were higher than comparable biosorbents or conventional materials, concluding that hemp fibers were a promising material for removing Ni from a single ion solution.

Another technique for the chemical modification of fibers consists of grafting functional ligands onto their surface, thanks to the high chemical reactivity of cellulose macromolecules. Thus, classical reactions in chemistry and the polysaccharide industry, such as esterification and carboxymethylation, can be applied. Cassano et al. (2013) prepared grafted fibers *via* esterification of hemp with 2-benzyl-4-chlorophenol that was covalently coupled to the cellulose backbone of fibers by a heterogeneous process. A detailed characterization by FT-IR spectroscopy and differential scanning calorimetry was used to obtain qualitative information on hemp fibers after grafting. Modified fibers had high adsorption capacities toward Cd present in aqueous solutions, but the performances for its removal were dependent on the solution pH. In addition, esterified fibers had a lower chelating capacity than those obtained with carboxylated fibers. The modified hemp fibers prepared by Cassano et al. (2013) were used not only for environmental applications but also in pharmaceutical and biomedical fields to prevent bacteria growth. Indeed, modified fibers possessed an excellent *in vitro* antibacterial activity in inhibiting *Staphylococcus aureus* and *Pseudomonas aeruginosa* growth.

Recently, Bai et al. (2020a, b) proposed modified hemp fibers for U extraction from seawater. In this report, the hemp fibers were pretreated with 8% NaOH solution to increase their hydrophilicity, followed by oxidation under acidic conditions to introduce a large number of carboxylic acid groups on the surface. Subsequently, polyethylenimine and guanidine acetic acid were covalently grafted onto the surface of the fibers (Bai et al. 2020a). The grafting reaction was demonstrated using infrared data. After treatment, EDX data indicated changes in the material's elemental composition, particularly a significant increase in the percentage of nitrogen element on the surface of fibers. The material was used as an amphoteric adsorbent to remove U present in simulated seawater by batch experiments, with a maximum adsorption capacity for U (VI) of 414.9 mg/g. However, the performance

was pH-dependent (optimum pH value of 7) due to the protonation of the amino group at lower pH, which generates electrostatic repulsion with the uranyl ion (UO_2^{2+}) and other uranium species in the solution. The novel green material also exhibited excellent selectivity and good regeneration performance. The kinetic and isotherm data modeling indicated that the biosorption process was mainly chemisorption (electrostatic attraction, coordination). A characterization using X-ray photoelectron spectroscopy (XPS) realized before and after uranium adsorption indicated strong interactions between U and the oxygen-containing functional groups of the material. A chemical complexation also occurred between the U ions and nitrogen-containing groups on the surface of the material. The conclusions were in agreement with kinetic and isotherm data. Moreover, the material presented good resistance to the algae adhesion even after 15 days. Experiments were performed in U solution containing algae after 1, 7, and 15 days of contact and at different temperatures to study the influence of marine microorganisms on adsorption capacity. Even after 15 days, a high efficiency (more than 72%) was obtained in all cases, indicating that the material's performance was not significantly affected. In another work, the same authors proposed hemp fibers functionalized with imidazole-4,5-dicarboxylic as biosorbents for U removal, reporting a maximum adsorption capacity for U (VI) of 469.4 mg/g at pH 7 (Bai et al. 2020b). The authors concluded that the two novel adsorbents had a good prospect for extracting U from seawater.

Núñez-Delgado's group studied the adsorption of Cr (VI) and fluoride ions on hemp wastes (Quintáns-Fondo et al. 2016, 2019; Romar-Gasalla et al. 2018), showing high capacities of hemp waste to adsorb fluoride ions and low for Cr (VI). Similar conclusions were obtained for competitive binary systems. However, an apparent competition between anionic elements was observed, with reductions in adsorption up to 90% for Cr (VI) and up to 30% for fluoride. The results reported that Cr (VI) presence hindered fluoride adsorption (Quintáns-Fondo et al. 2019). Biosorption data also showed better fitting to the Freundlich than to the Langmuir model, especially in the case of Cr (VI), indicating that multilayer biosorption dominated. Núñez-Delgado's group also studied the adsorption of As (V) on hemp wastes, but adsorption capacities were low (Quintáns-Fondo et al. 2017). Detailed modeling of the experimental data indicated a low probability of easy saturation of biosorption sites during the biosorption process.

3.3 *Hemp-Based Felts*

Crini's group was the first to propose the use of a hemp-based material in the felt form to treat polymetallic aqueous synthetic solutions and polycontaminated real effluents from the surface treatment industry (Bugnet et al. 2017a, b; Loiacono et al. 2017a, b, c, 2018a, b; Morin-Crini et al. 2019, 2020; Crini et al. 2021). The metals studied were Pb, Cd, Cu, Zn, Co, Ni, Fe, Cr, Al, and Mn. They were chosen due to their common presence in effluents discharged from the metal industry. Biosorption

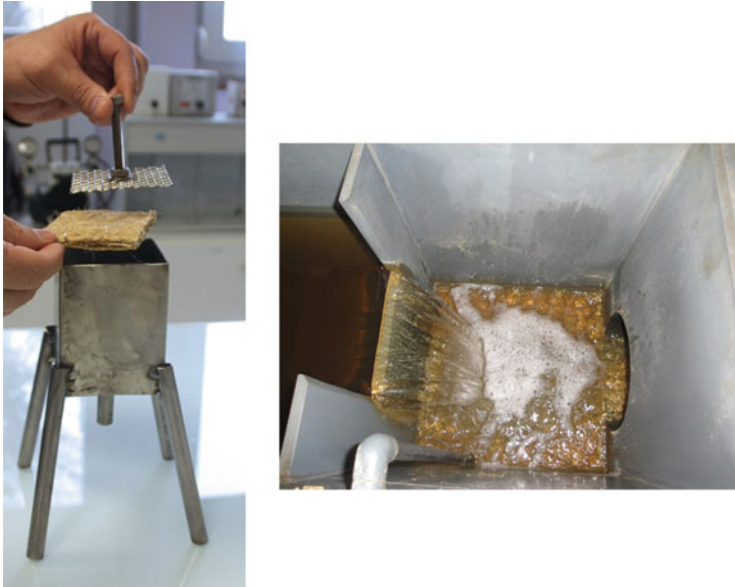


Fig. 4 A device used during filtration-adsorption tests: laboratory scale (left) and industrial pilot (right). Copyright G. Crini

results were obtained using batch protocols and filtration-adsorption experiments using the equipment presented in Fig. 4.

Under controlled batch conditions (volume of solution = 100 mL, felt dose = 1 g, contact time = 60 min, pH = 5 and metal concentration = 1–300 mg/L), biosorption results showed that the felt had high adsorption capacities toward metals in the following order: Pb > Cd > Cu > Zn > Co ~ Fe ~ Ni ~ Cr ~ Al ~ Mn. With an initial concentration of 25 mg/L, the abatement values for Pb, Cd, Cu, Zn, Co, Ni, Fe, Cr, Al and Mn were 96%, 88%, 84.5%, 77%, 70%, 68%, 67%, 67%, 66% and 63%, respectively. At any concentration, the same order of reduction was obtained for all metals studied. Pb, Cd, and Cu showed the highest affinity, whereas Mn demonstrated the lowest level of removal. The difference in the degree of adsorption was attributed to each metal's physical and chemical characteristics such as ionic radius, electronegativity, and molar mass. As expected, biosorption efficiency decreased with the increase of the metal concentration due to the saturation of the biosorption sites on the material. In contrast, experimental data also indicated that the biosorption efficiency improved considerably with the increase of the biosorbent dosage and the performance was independent of pH between 4–6. However, at pH lower than 3, the reductions decreased drastically due to the competition of H⁺, except for Pb and Cu. A similar trend was reported for the adsorption of Ag, Cd, Co, and Zn by hemp fibers by Păduraru and Tofan (2008), Rezić (2013), Pejić et al. (2009, 2011), and Tofan et al. (2013, 2015). Crini's group also studied kinetics obtained with hemp-based materials in felt form. Kinetic data demonstrated that the



Fig. 5 Hemp before (a) and after biosorption in a solution containing copper (b), cobalt (c) or blue dye (d). Copyright G. Crini

biosorption process was rapid, 10 min sufficient to attain equilibrium for the metals studied. Langmuir model calculates the following q_{\max} values: 27.47, 14.64, 10.59, 7.99, 7.85, 7.87, 6.53, 6.38, and 4.55 mg/g for Cd, Cu, Zn, Co, Fe, Ni, Cr, Al, and Mn, respectively. These materials were also capable of adsorbing dyes. Figure 5 illustrates the coloring of the felt after metal and dye removal using real effluents.

The potential of using a hemp-based material in the felt form to treat polymetallic aqueous solutions containing a mixture of six metals (Cd, Co, Cu, Mn, Ni, and Zn) was also assessed for the first time. 1 g of hemp could remove 7.4 mg of metals at a concentration of 25 mg/L for each metal present in 100 mL of solution. From a kinetic perspective, the process was uniform and rapid, with a similar equilibrium time (10 min) as obtained for the monometallic solution. For the concentration range studied between 1 and 100 mg/L for each metal, the lowest level of removal of the felt was obtained for Mn (between 75.6% and 1.7%), whereas the highest affinity was obtained for Cu (between 95% and 42%). The adsorption capacities were almost independent of temperature between 25 and 50 °C and of pH between 4 and 6 but dependent on the presence of electrolytes such as NaCl. However, a change in the order of biosorption was obtained for the mixture compared to single solutions. In mixtures, independently of the operating variables studied, the following order was obtained: Cu >> Cd > Zn > Ni ~ Co > Mn, while, in a single solution, the order was Cd > Cu > Zn > Co ~ Ni > Mn.

Tests with real effluents containing 14 metals (Al, Cd, Co, Cu, Cr, Fe, Li, Mn, Ni, Pb, Sn, Sr, Ti, and Zn) in a concentration range between 0.16 and 22.3 mg/L depending on the metal were carried out. The results showed that high levels of metal removal were achieved using hemp (in most cases 75–80% of the metal load), reaching values well below the water quality criteria for industrial discharges, the so-called “close to zero discharge.” The felt could remove substances other than metals, *i.e.*, inorganic substances (S, B, etc.) and organic pollutants (chloroform, 1,2-dichlorobenzene, nonylphenol, etc.). Standardized ecotoxicological tests based on the mobility of *Daphnia magna* also confirmed the efficiency of the biosorption to decrease the effluent toxicity. To evaluate changes in the surface morphology of the biosorbent before and after biosorption, and to highlight the adsorption mechanism, SEM images and EDX spectra were analyzed. SEM images indicated changes in the morphology of hemp after biosorption (Fig. 6). SEM and EDX studies of raw and loaded biosorbent also confirmed the involvement of precipitation in the biosorption process.

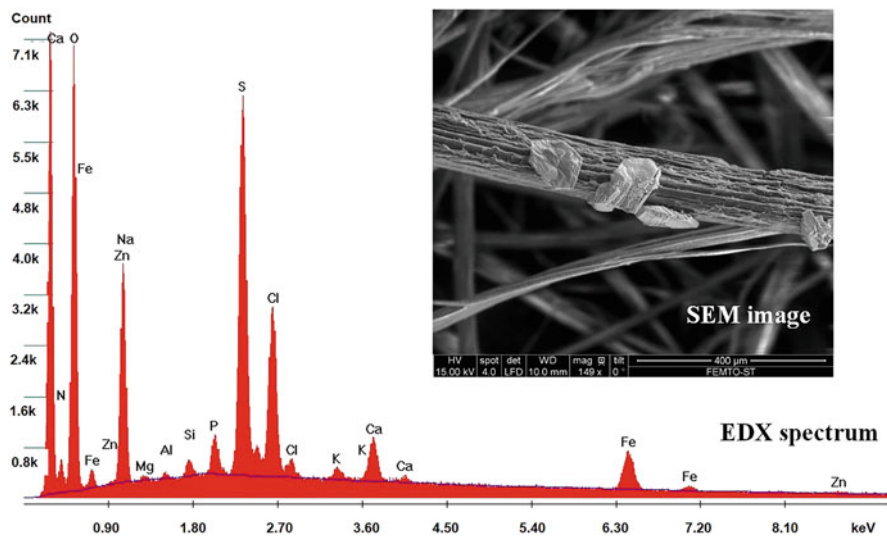


Fig. 6 Scanning electron microscopy (SEM) image and elemental analysis using energy-dispersive X-ray spectroscopy (EDX) spectrum of the felt after biosorption of the pollutants present in an industrial effluent polycontaminated and particularly concentrated in zinc, iron, and aluminum. The SEM image (400 μm) shows agglomerates at the surface of the fiber. This image was obtained using a scanning electron microscope, Apreo, ThermoFisher Scientific, with a tungsten filament voltage from 15 keV to 20 keV and low-vacuum conditions. The EDX spectrum was performed using the Thermo NORAN system for energy-dispersive X-ray spectroscopy and the electron beam excitation with a voltage from 15 keV to 20 keV

Loiacono et al. (2017a, b) proposed a chemical modification of raw felt to increase its biosorption by introducing carboxylic groups on hemp fibers. The felt was modified using an esterification reaction by a cross-linking reaction between 1,2,3,4-butane tetracarboxylic acid (BTCA) in the presence of maltodextrin (MALTO), an oligosaccharide obtained from starch hydrolysis. The chemical structures of BTCA and MALTO are shown in Fig. 7. BTCA is used as a cross-linking agent permitting esterification between its carboxylic groups and MALTO hydroxyl groups, and cellulose hydroxyl groups of hemp fibers (Loiacono et al. 2017b). Another aim was to reduce surface polarity by chemically modifying the hydroxyl groups. The felts before and after modification were characterized by solid-state ^{13}C -nuclear magnetic resonance (NMR) (Fig. 7), allowing to verify the grafting of carboxylic groups. Moreover, a 35% weight increase of modified felt also confirmed the modification. Acidic properties were characterized using a simple potentiometric titration (Ducoroy et al. 2007), which permitted obtaining a value of ion-exchange capacity (IEC expressed in mg/g) of the materials. Data revealed that the quantity of carboxylic groups increased from 0 ± 0.09 meq/g for raw felt to the range $0.3\text{--}1.0 \pm 0.09$ meq/g for modified felt.

Biosorption data showed that for both synthetic solutions and real effluents, the adsorption capacity of modified hemp to remove the total metal load was two-fold

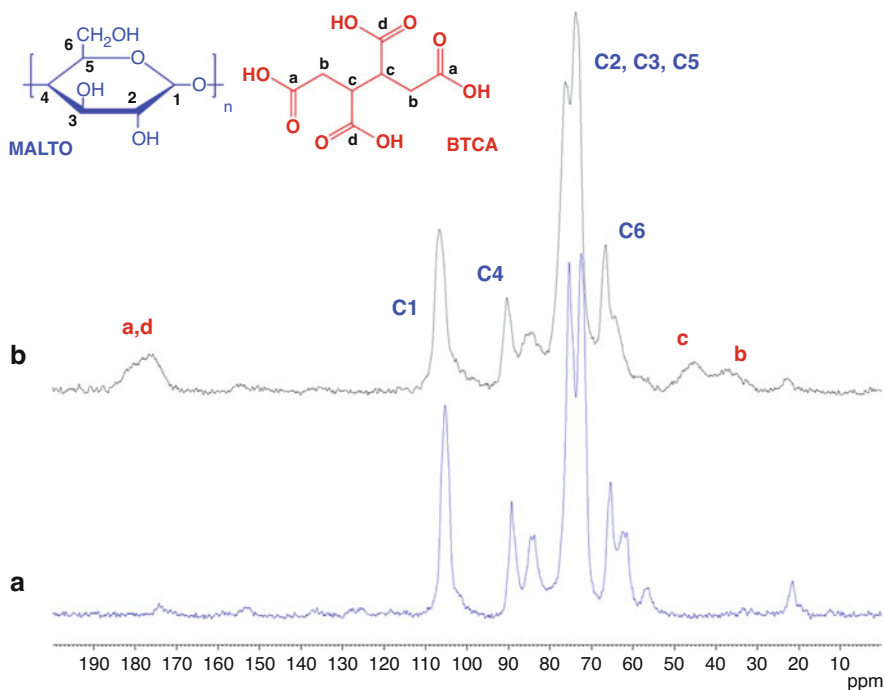


Fig. 7 Cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectra of raw hemp felt (**a**) and modified hemp felt (**b**). Solid-state ^{13}C NMR spectra show the peaks of disordered cellulose (C1-C6 peaks of the glucopyranose unit in the range 50–110 ppm). Additional peaks are present in the spectrum of modified felt: a large band at 170–180 ppm (carboxylic groups) and peaks between 30 and 50 ppm. The spectra were recorded with a Bruker Avance HD spectrometer operating at 125 MHz

higher than that of non-modified felt under all conditions studied (Loiacono et al. 2017a). NMR, SEM, and EDX data confirmed that the carboxylic groups were responsible for metal ion binding through chemisorption mechanisms, *e.g.*, complexation, electrostatic interactions, ion-exchange, and microprecipitation. Industrial-scale tests were also carried out using the pilot in Fig. 4 to validate the laboratory studies (Morin-Crini et al. 2019, 2020; Crini et al. 2021). Crini's group concluded that raw and modified hemp-based materials in felt form could be utilized as an alternative for the purification of metal-containing wastewater because of their outstanding adsorption capacities, ease of use, and ability to decrease the effluent toxicity. The same modified felts have been used recently to limit the diffusion of fungicides in vegetable garden soils (Léchenault-Bergerot et al. 2019; Godeau et al. 2021).

3.4 Shives for Copper Removal

The potential of using hemp shives in granular form as biosorbents for removing copper was investigated by Balintova et al. (2014). Raw shives were treated with NaOH to remove either hemicelluloses or lignin and produce carboxylate groups by saponification. The adsorption capacities for raw and treated hemp were 3.91 and 4.45 mg/g, respectively, in batch experiments performed at an initial pH of 4 (other conditions were: dosage = 1 g/100 mL; initial Cu concentration = 50 mg/L, contact time = 24 h). These performances were compared with those of commercial sorbents, and similar adsorption capacities were observed. Adsorption and kinetic data indicated that the carboxyl groups played an important role in the binding of metal ions. The authors concluded that hemp shives were a low-cost and useful non-conventional biosorbent for Cu removal from an acidic environment (Balintova et al. 2014; Številová et al. 2014).

A similar conclusion was recently published by Rozumová's group (Rozumová et al. 2018; Rozumová and Legátová 2018). Shives were washed with a 0.1 mol/L solution of HCl to remove impurities, while carboxyl groups were introduced. The q_{\max} for Cu was determined to be 5.48 mg of the metal per gram of material. Their results also showed that the biosorption process was uniform and rapid, with the removal equilibrium of Cu being reached in 60 min under the optimum pH of 5. The mechanism was explained with the Langmuir type I model, suggesting forming a metal monolayer on the biosorbent surface. The kinetics showed that a pseudo-second-order equation better fitted the experimental data. According to these authors, activated hemp shives can be used as a low-cost, ecofriendly adsorbent for Cu removal with high efficiency (Rozumová et al. 2018; Rozumová and Legátová 2018).

Crini's research group also prepared hemp materials in the form of shives using the same procedure used to modify hemp in the form of felts. Thus, raw shives (called SHI-R) were modified with BTCA to provide ion-exchange properties to the biosorbent by introducing carboxylic groups using the same method published by Loiacono et al. (2017b). The weight increase of 15–20% of modified shives (called SHI-BTCA) confirmed that an esterification reaction occurred between BTCA carboxylic groups and cellulose hydroxyl groups of hemp. Similar to the material in felt form, the potentiometric titration data showed that the quantity of carboxylic groups increased after BTCA treatment. The IEC values were 0.10 ± 0.09 meq/g and 1.5 ± 0.2 meq/g for SHI-R and SHI-BTCA, respectively. The N₂ adsorption/desorption isotherms were performed by pre-treating the samples at 80 °C for 180 min (Rachini et al. 2012; De Vietro et al. 2011, 2012, 2019; Dizbay-Onat et al. 2018). Table 4 reports the obtained results. Both for SHI-R and SHI-BTCA samples, the same high BET and pore surface area were observed, features required to obtain high efficiency of pollutant removal. Moreover, significant differences for the pore radius, volume, and surface area for both samples were not detected, indicating that the reaction with BTCA did not affect the features of SHI-R. Overall, the values of the pore radius obtained suggested that both samples can be classified

Table 4 Porous properties of raw (SHI-R) and modified (SHI-BTCA) hemp shives

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	Pore surface area ^b (m^2/g)	Pore volume ^b (cm^3/g)	Pore radius ^b $D_v(r)$ (\AA)
SHI-R	9.33 ± 0.08	6.821	0.036	15.655
SHI-BTCA	8.60 ± 0.07	6.765	0.060	15.640

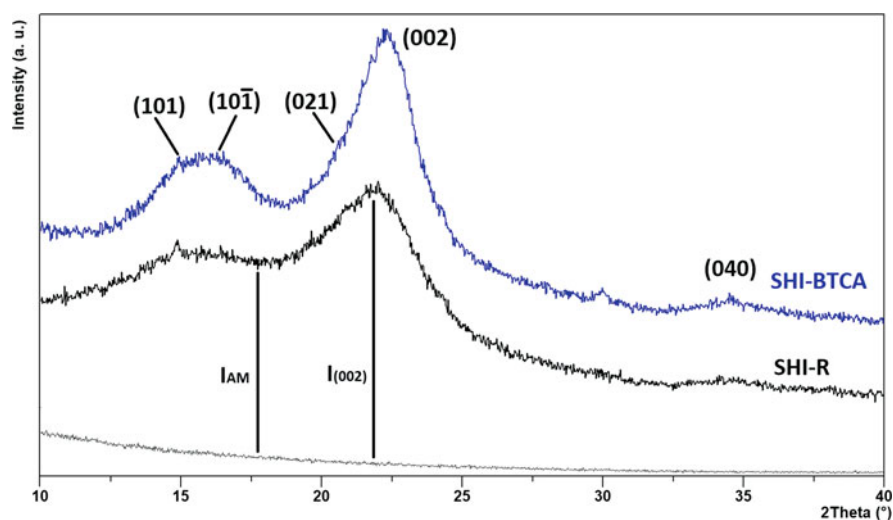
^a Brunauer-Emmett-Teller (BET) surface area^b Using the Barrett-Joyner-Halenda (BJH) method

Fig. 8 A detail from $2\theta = 5$ to 40° of X-ray diffraction (XRD) patterns of raw shives (SHI-R) and modified shives (SHI-BTCA) samples. These figures illustrate the main features of the patterns and the method used for calculating the crystallinity index. The SHI-BTCA pattern is shifted with respect to SHI-R. The thin black line represents the background. XRD data were collected in the air using a Panalytical Empyrean X-ray diffractometer operating at 40 kV/40 mA with $\text{CuK}\alpha$ radiation, Bragg-Brentano geometry, large beta filter-Nickel, PIXcel3D detector. The diffraction patterns were processed using the Panalytical B.V. software High Score Plus version 3.0e

as mesoporous biosorbents. Thus, the BTCA treatment did not modify the morphology of the modified material.

Figure 8 shows the XRD pattern of SHI-R and SHI-BTCA samples with detail from $2\theta = 5$ to 40° . The well-known diffraction peaks at 2θ around 14.5° , 16.5° , and 22.0° were attributed to the cellulose reflections 101, $10\bar{1}$ and 002, respectively, in agreement with the data reported by Park et al. (2010b). The treatment of the hemp fibers did not cause significant structural variations, considering that only slight peak shifts towards higher 2θ angles related to the decrease of the interplanar distance of the cellulose's planes were observed. However, the intensity of the diffraction peak at $2\theta \approx 30^\circ$ was increased after the treatment. Similar behavior was already observed for hemp particles after wet milling (Zhang et al. 2020b) due to the lower preferential orientation of the cellulose fibers (French 2014). The intensities in the 2θ range from

5° to 40° were used to calculate the crystallinity index of the samples according to the Eq. (4) (Segal et al. 1962) where I_{002} is the height of the diffraction peak located at 2θ around 22.0° and corresponding to the cellulose crystalline domain, while I_{AM} is the minimum diffraction intensity located between (002) and (10 $\bar{1}$) peaks, at $2\theta \approx 18^\circ$, corresponding to the amorphous domain, after subtracting the background signal measured without sample as suggested by Park et al. (2010b). The crystallinity indexes of untreated and treated hemp were 28.1% and 48.8%, respectively. Therefore, the treatment has increased the crystallinity index of hemp particles, likely due to the re-organization of the structure (Wang et al. 2003; Hakamy et al. 2015).

$$CI = \frac{I_{002} - I_{AM}}{I_{002}} \times 100\% \quad (4)$$

The introduction of carboxylic groups on the surface of the materials is also demonstrated from NMR (Fig. 9) and infrared (Fig. 10) spectroscopy data. Comparing the CPMAS spectra of SHI-R and SHI-BTCA shows an additional broad signal between 170 and 180 ppm in the spectrum of SHI-BTCA, ascribed to the carboxylic groups (Fig. 9). Other peaks in the range of 50–110 ppm can be assigned to the glucopyranose unit present in the cellulose structure of the shives. The spectra also show peaks due to the presence of residual lignin and/or impurities, which has been confirmed by chemical analysis using the Soutar and Bryden procedure (Garner 1967). SHI-BTCA contains $36.58 \pm 1.89\%$ α -cellulose (expressed in w/w), $12.57 \pm 1.24\%$ hemicelluloses, 39.6% lignin, $3.21 \pm 0.92\%$ pectins, 0.76 ± 0.39 fats and waxes, and $7.29 \pm 0.12\%$ water solubles, while SHI-R contains $55.53 \pm 0.27\%$ α -cellulose, $12.48 \pm 0.33\%$ hemicelluloses, 26.54% lignin, $0.43 \pm 0.53\%$ pectins, 0.72 ± 0.72 fats and waxes, and $4.30 \pm 0.49\%$ water solubles. It is well-established that the fibers contain more cellulose and less lignin and hemicelluloses, while shives contain less cellulose and more lignin and hemicelluloses. Lignin binds to hemicelluloses since hemicellulose hydroxyl groups are much more accessible to lignin than cellulose (Thomsen et al. 2005). In the infrared spectra (Fig. 10), the main differences in absorption band height were observed in the fingerprint region below 1500 cm^{-1} . The region between 4000 and 1800 cm^{-1} presents two important bands at 3420 cm^{-1} (H-bonded of hydroxyl groups; OH stretching for cellulose and hemicelluloses) and 2920 cm^{-1} (C-H stretching of CH_2 groups). The peaks in the region 1500 – 1800 cm^{-1} were assigned to the absorption of carboxylate (at 1580 and 1600 cm^{-1} for SHI-BTCA and SHI-R, respectively) and carboxyl (at about 1725 and 1730 cm^{-1} for SHI-BTCA and SHI-R, respectively) groups, and the bands were more intense for the SHI-BTCA sample than for SHI-R sample. Min et al. (2004) and Dai and Fan (2010) reported similar spectra and conclusions. Figure 11 shows EDX spectra and SEM images obtained for the two samples. The data analysis indicated that the chemical modification significantly changed the morphology and roughness of the material surface. The elements that composed the surface were mainly carbon, oxygen, potassium, calcium for SHI-R,

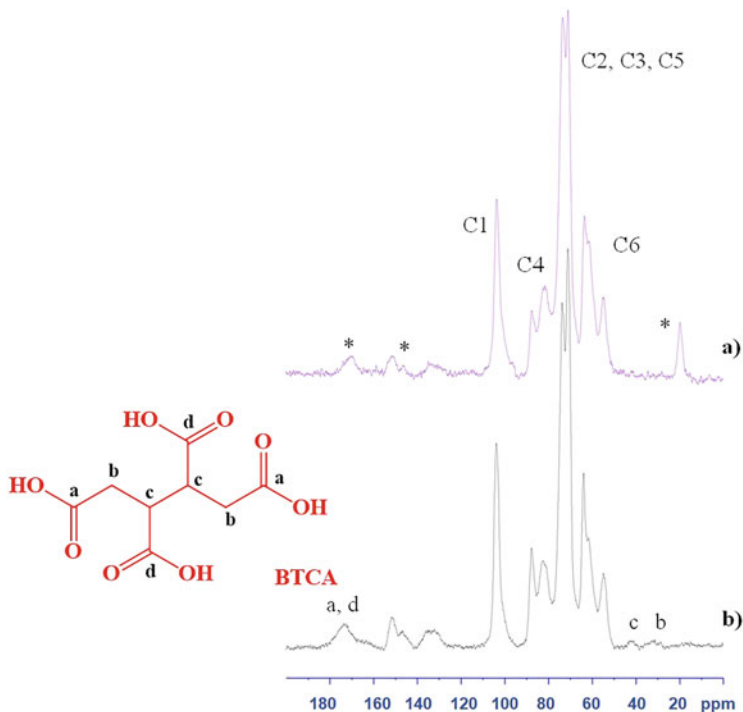


Fig. 9 Cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectra for (a) raw shives and (b) modified shives samples by using 1,2,3,4-butane tetracarboxylic acid (BTCA). Solid-state ^{13}C -NMR spectra show the peaks of disordered cellulose (C1–C6 peaks of the glucopyranose unit in the range 50–110 ppm) and other peaks (marked with an *) due to residual lignin and/or impurities (a) and a large band at 170–180 ppm due to the carboxylic groups, indicating the grafting of BTCA (b). The spectra were recorded with a Bruker Avance HD spectrometer operating at 125 MHz

carbon, oxygen, and sodium (present in the activated carboxylate groups) for SHI-BTCA.

The results in Fig. 12 compare the performance of raw shives (SHI-R) and shives modified with BTCA (SHI-BTCA) to adsorb Cu at different metal concentrations, ranging from 5 to 300 mg/L. The data indicate that the modified shives are more efficient than the non-modified shives independently of the initial metal concentration, pointing out the important role of the carboxylic groups in the biosorption mechanism. Up to 100 mg/L, the efficiency of SHI-BTCA was remarkable since the removal was complete (~100%). The results for SHI-R are also interesting because, up to 100 mg/L, the removal of Cu was in the range of 60–55%, indicating good affinities between the raw shives and the Cu cations. As expected, biosorption efficiency decreased for both the materials when the Cu concentration increased, suggesting the saturation of the biosorption sites on the material. It is important to note that a slight pH variation between 0.5 and 0.9 units for the SHI-BTCA sample was observed at the end of each experiment, indicating a chemisorption mechanism.

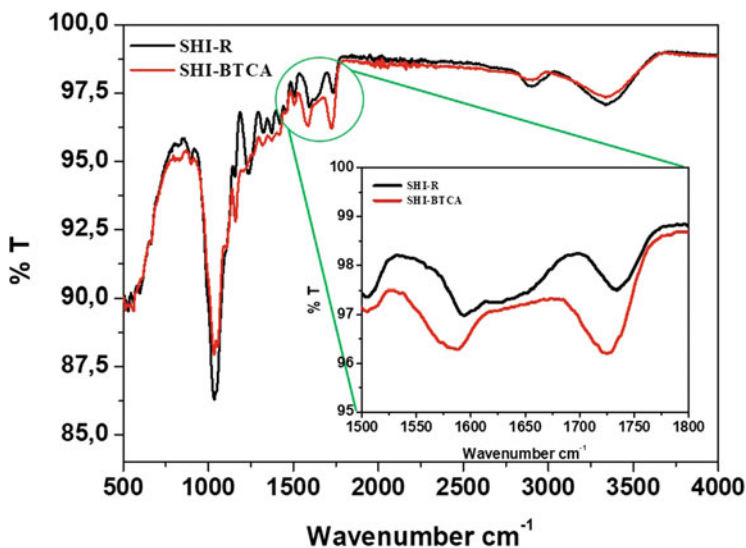


Fig. 10 Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra of raw shives (SHI-R) and modified shives (SHI-BTCA) samples by using 1,2,3,4-butane tetracarboxylic acid (BTCA). Spectra were recorded on a Perkin Elmer spectrometer (FTIR Spectrum Two, Waltham, MA, USA)

The results of the adsorption of Cu on both biosorbents by changing the quantity of material at different initial metal concentrations are compared in Fig. 13. As expected, for both materials, when the quantity of material increases, the percentage of removal increases. Again, it is interesting to note the high levels of reduction obtained for SHI-BTCA compared to SHI-R. Setting SHI-BTCA doses at 3 g/100 mL in the batches resulted in an almost complete Cu removal regardless of the initial metal concentration.

The equilibrium data can be analyzed using the classical models described in Table 5 to establish the most appropriate correlation for the equilibrium curve. The correlation of experimental data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems. The different equation parameters and the presuppositions of the models can provide insight into both the adsorption mechanism and the surface properties and affinity of the material (Tien 1994; Hamdaoui and Naffrechoux 2007; Crini and Badot, 2010; Vandebossche et al. 2015; Tran et al. 2017; Crini and Lichtfouse 2019c; Al-Ghouti and Da'ana 2020; Beni and Esmaili 2020).

Figure 14 compares the measured and modeled profiles for Cu adsorption by the two samples using six isotherms. Table 6 compares the values of non-linear regression coefficients of determination (r^2) and the chi-square test statistic (χ^2) for the six models. The main results are the following. The comparison of error analysis showed that the best fitting order was Redlich-Peterson > Generalized > Toth > Langmuir > Temkin > Freundlich for SHI-R sample, and

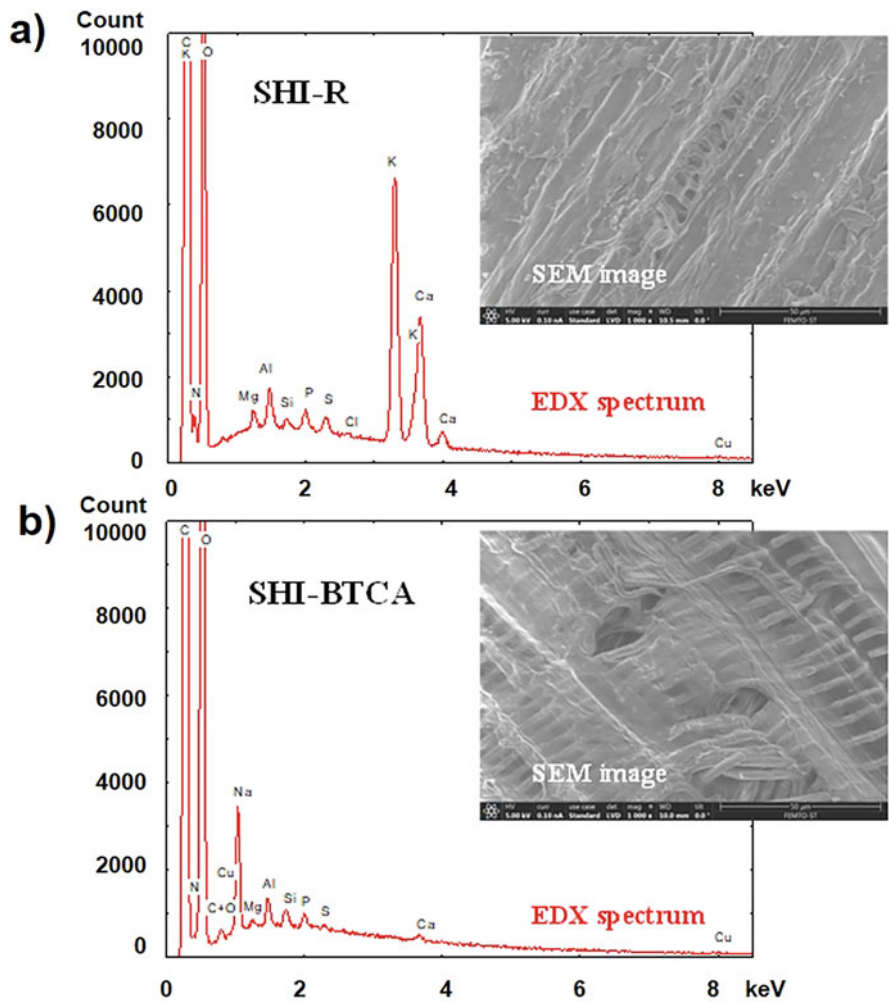


Fig. 11 Elemental analysis using energy-dispersive X-ray (EDX) spectra and scanning electron microscopy images (SEM) of raw shives (SHI-R) (a) and modified shives (SHI-BTCA) (b) samples by using 1,2,3,4-butane tetracarboxylic acid (BTCA). EDX spectra were performed using the Thermo NORAN system for energy-dispersive X-ray spectroscopy and the electron beam excitation with a voltage from 15 keV to 20 keV. SEM images (50 μ m) were obtained using a scanning electron microscope, Apreo, ThermoFisher Scientific, with a tungsten filament voltage from 15 keV to 20 keV and low-vacuum conditions

Tempkin > Generalized > Redlich-Peterson > Toth > Freundlich > Langmuir for SHI-BTCA sample. For the raw shives, examining the non-linear plots suggested that the Redlich-Peterson model yielded a much better fit than the other models. The

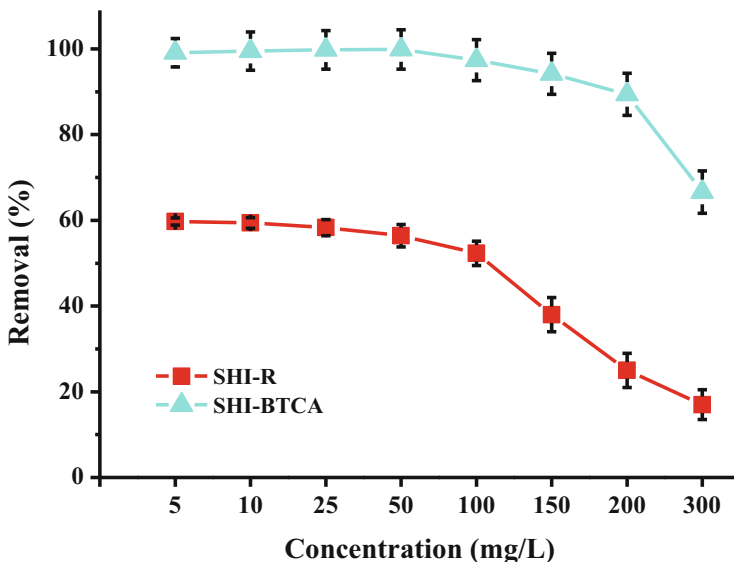


Fig. 12 Effect of initial metal concentration (mg/L) on the removal of copper (expressed in %) onto two hemp shives, SHI-R (raw shives) and SHI-BTCA (modified shives); (other conditions: adsorbent dose 2 g; volume of solution 100 mL; contact time 120 min; agitation speed 250 rpm; temperature 22 ± 1 °C; pH 5 ± 0.1 ; n = 3)

χ^2 values for this model are small, indicating that the data from the model are similar to the experimental data. The Redlich-Peterson isotherm combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is hybrid and does not follow ideal monolayer adsorption. This empirical model describes the equilibrium over a wide range of concentrations, applicable in either homogeneous or heterogeneous processes. The Tempkin model yielded the best fit for the modified shives, suggesting an ion-exchange mechanism, considered as physical adsorption. This model mainly considers the interaction between the pollutant and the material, which causes a linear decrease in the biosorption heat (a function of temperature) with a coverage linear rather than logarithmic. This implies that the binding energies are uniformly distributed.

The q_{\max} values were 2.87 mg/g and 10.1 mg/g for SHI-R and SHI-BTCA, respectively. The value for SHI-BTCA is two times higher than that obtained by Rozumová et al. (2018). The Freundlich model permits obtaining a heterogeneity factor ($1/n_F$) characteristic of the pollutant-biosorbent system, which indicates the degree of non-linearity between solution concentration and adsorption (Crini and Badot 2010; Tran et al. 2017; Al-Ghouti and Da'ana 2020). If the value of $1/n_F$ is below unity, this implies that the adsorption process is chemical, and the closer the $1/n_F$ value is to 0, the more heterogeneous the surface is. The values were 0.61 and 0.37 for SHI-R and SHI-BTCA, respectively, indicating favorable adsorption.

To evaluate the changes in the materials' surface morphology and confirm the chemisorption mechanism, the samples after Cu adsorption were also examined by

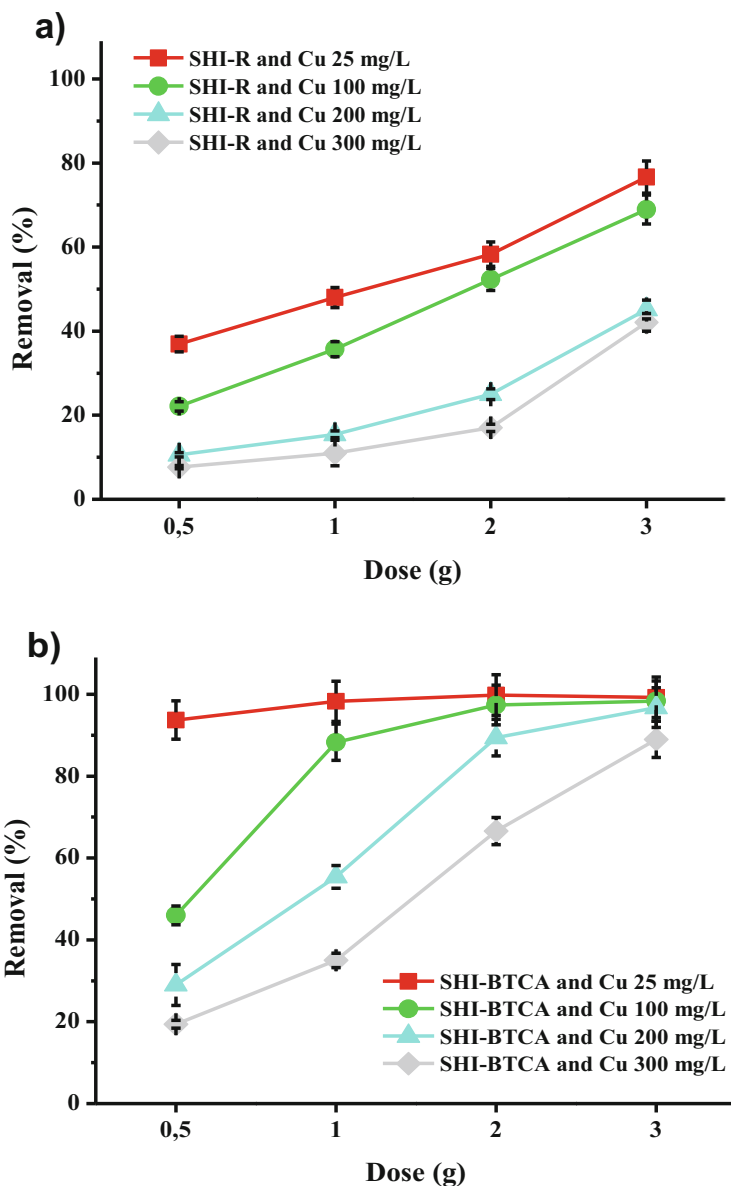


Fig. 13 Comparison of the metal removal (%) with increasing doses of (a) SHI-R (raw shives) and (b) SHI-BTCA (modified shives) adsorbents using a different initial copper concentration in the range 25–300 mg/L; (other conditions: volume of solution 100 mL; contact time 120 min; agitation speed 250 rpm; temperature 22 ± 1 °C; pH 5 ± 0.1 ; n = 3)

Table 5 Six common types of isotherms used in the literature

Isotherms	Non-linear equation	Linear equation	Reference
Langmuir	$q_e = \frac{K_L C_e}{1 + a_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e$	Langmuir (1916)
Freundlich	$q_e = K_F C_e^{1/n_F}$	$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$	Freundlich (1906)
Tempkin	$q_e = \frac{RT}{b} (\ln A C_e)$	$q_e = \left(\frac{RT}{b}\right) \ln A + \left(\frac{RT}{b}\right) \ln C_e$	Tempkin (1940)
Generalized	$q_e = q_{max} \frac{C_e^n}{K + C_e^n}$	$\ln \left[\frac{q_{max}}{q_e} - 1 \right] = \ln K - n \ln C_e$	Kargi (2004)
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$	$\ln \left[\frac{K_R C_e}{q_e} - 1 \right] = \ln a_R + \beta \ln C_e$	Redlich and Peterson (1959)
Toth	$q_e = \frac{K_T C_e}{[a_T + C_e]^i}$	$\ln \left[\frac{q_e}{K_T} \right] = \ln C_e - \frac{1}{i} \ln (a_T + C^i)$	Toth (1971)

SEM and EDX spectroscopy (Fig. 15). The analysis of the EDX spectrum showed a decrease in the concentration of the Na⁺ cations coupled with an increase in the concentration of the Cu cations. The SEM image showed agglomerates at the sample's surface, confirming the involvement of precipitation in the biosorption process. Comparing the ATR-FTIR spectra before and after biosorption for the SHI-BTCA sample also showed significant differences in the 1500–1800 cm⁻¹ range (Fig. 16). No displacement was observed for the 1725 cm⁻¹ band corresponding to the carboxyl group, while the 1580 cm⁻¹ band underwent a profound change in both intensity and width, reflecting the implication of the carboxylate groups on the Cu ions sequestration. The comparison between the CPMAS spectra of the same samples before and after metal adsorption also showed a chemical shift modification for the BTCA signals. All these IR and NMR data prove the involvement of a chemisorption mechanism. Based on the presented results and in agreement with other studies (Balintova et al. 2014; Številová et al. 2014; Rozumová et al. 2018), it can be assumed that the modified hemp shives have a metal biosorption potential.

3.5 Composite Materials

The interaction between a hemp-zeolite composite material and aromatic organic pollutants such as benzene, toluene, and chlorobenzene, was investigated by Zou et al. (2012). The material was prepared *via in situ* crystallization of zeolite L nanocrystals on hemp fibers and characterized by XRD and SEM data. The pollutant biosorption onto the composite material was spontaneous. Performances were high, above 80%, and the order obtained was: chlorobenzene > benzene > toluene. The composite also presented a high flux of 19.9, 19.3, and 20.9 kg/m²h for chlorobenzene, benzene, and toluene, respectively. The results showed that the removal efficiency of the composite was much higher than that of hemp fibers (48%) due to an improved absorption ability of the zeolite-hemp material coupled with higher dynamic separation efficiency. After regeneration and several cycles of biosorption/

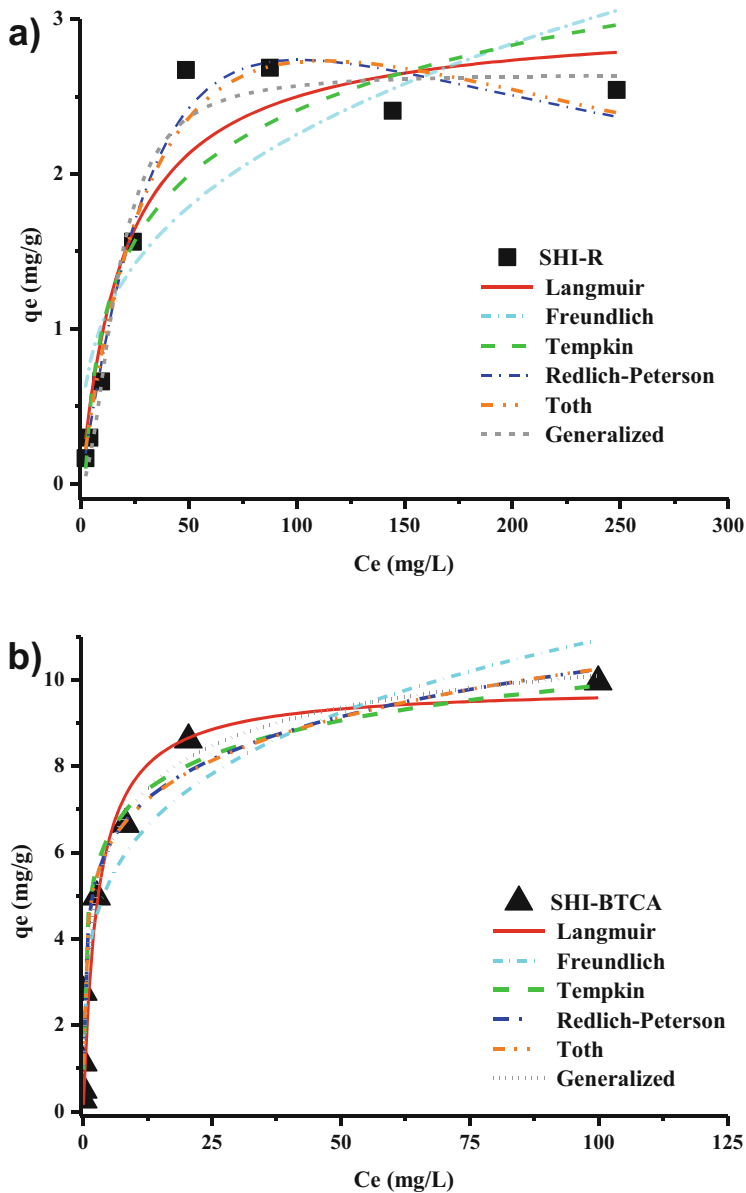


Fig. 14 Comparison of Langmuir, Freundlich, Temkin, Generalized, Redlich-Peterson, and Toth isotherms for copper adsorption onto **(a)** SHI-R (raw shives) and **(b)** SHI-BTCA (modified shives) samples (other conditions: adsorbent dose 2 g; a volume of solution 100 mL; agitation speed 250 rpm; temperature 22 ± 1 °C; pH 5 ± 0.1 ; n = 3)

Table 6 Comparison of non-linear regression coefficients of determination (r^2) and the chi-square test statistic (χ^2) (the chi-square test is the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models)

Shives	Isotherm	r^2	χ^2
	Langmuir	0.9151	0.1032
	Freundlich	0.7295	0.3287
SHI-R	Tempkin	0.8665	0.1623
	Generalized	0.9594	0.0493
	Redlich-Peterson	0.9677	0.0393
	Toth	0.9569	0.0524
	Langmuir	0.9024	1.3898
SHI-BTCA	Freundlich	0.9073	1.3212
	Tempkin	0.9486	0.7327
	Generalized	0.9454	0.7780
	Redlich-Peterson	0.9388	0.8724
	Toth	0.9381	0.8821

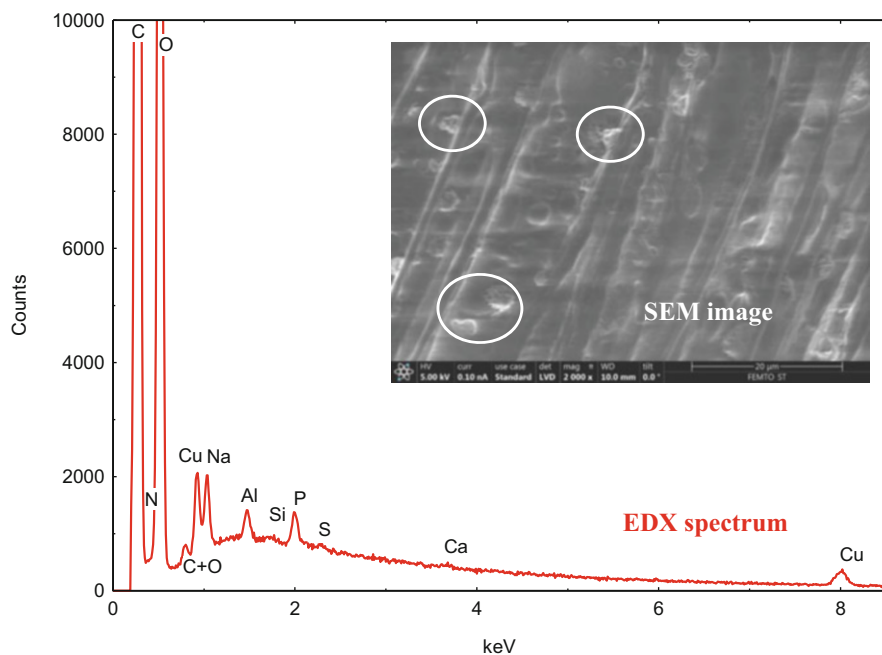


Fig. 15 Scanning electron microscopy (SEM) image and energy-dispersive X-ray spectroscopy (EDX) spectrum of SHI-BTCA (modified shives) after copper adsorption (initial metal concentration = 100 mg/L, adsorbent dose = 2 g). The SEM image (20 μ m) shows agglomerates at the surface of the sample. The SEM image was obtained using a scanning electron microscope, Apreo, ThermoFisher Scientific, with a tungsten filament voltage from 15 keV to 20 keV and low-vacuum conditions. The EDX spectrum was performed using the Thermo NORAN system for energy-dispersive X-ray spectroscopy and the electron beam excitation with a voltage from 15 keV to 20 keV

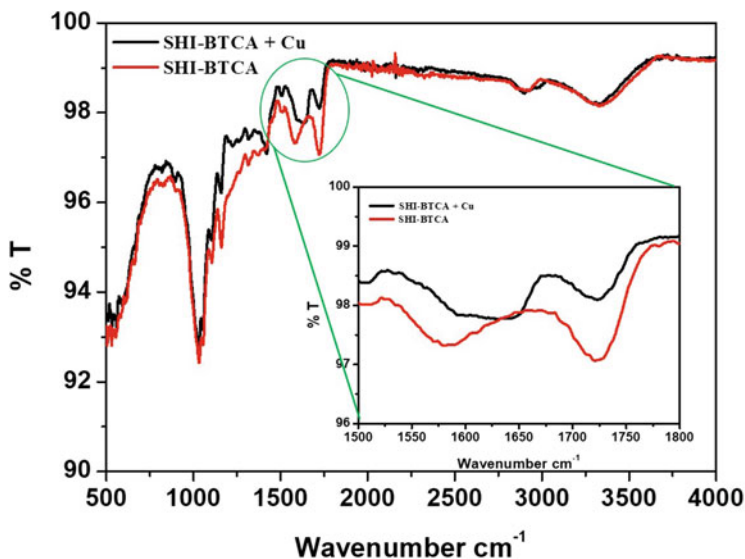


Fig. 16 Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of SHI-BTCA (modified shives) before and after copper adsorption (initial metal concentration = 100 mg/L, adsorbent dose = 2 g/100 mL). Spectra were recorded on a Perkin Elmer spectrometer (FTIR Spectrum Two, Waltham, MA, USA)

desorption, the composites maintained their pollutant removal efficiency (>80%). The authors concluded that the composite was particularly appropriate for water purification due to its intrinsic properties (mechanical and chemical stabilities under various conditions), outstanding biosorption performance, and reusability (Zou et al. 2012).

3.6 Hemp Plant Proteins

Using hemp protein powder, Turner et al. (2019) proposed novel remediation of per- and polyfluoroalkyl substances from contaminated groundwater. High reductions (>98%) were obtained, and kinetics were rapid: the highest performances were obtained within 1 h of contact time. When normalized for protein content, hemp removed pollutants more efficiently than soy, lupin, whey, pea, and egg proteins. In the presence of hemp protein powder, increasing salinity appeared to favor pollutant removal. An ATR-FTIR demonstrated the presence of strong hydrogen bonding and hydrophobic interactions during the biosorption process. This spectroscopic technique was also useful to determine changes in the protein structure. Turner et al. (2019) concluded that, unlike commercial carbons, hemp protein powders consist of a natural, low-cost product that does not require pyrolysis to make it an efficient

adsorbent. Hemp protein appeared to be ~2.7 times cheaper than treatment with an equivalent dose of Norit[®] granular activated carbon.

4 Activated Carbons from Hemp

4.1 *Activated Carbons in Wastewater Treatment: Why Innovate?*

Because of their great capacity to adsorb pollutants, *e.g.*, pesticides, phenols, dyes, and metals, to decrease chemical oxygen demand, biochemical oxygen demand, and total organic carbon, and to eliminate odors, commercial activated carbons are one of the oldest and the most widely used adsorbents. Activated carbons' adsorption capacities are mainly due to their structural characteristics and porous texture and their chemical nature (especially surface functional groups) that can be easily modified by different chemical treatments. So, commercial activated carbons are preferred conventional adsorbents for pollutant removal. However, their widespread industrial use is restricted due to the high cost of the starting material/precursor (such as petroleum residues, wood, coal, and some commercial polymers) (Radovic et al. 2000; Crini, 2006; Yahya et al. 2015; Ahmed 2016). Another disadvantage of commercial activated carbons is their rapid saturation that imposes the necessity for their regeneration and/or incineration. The latter approach is often preferred because regeneration is expensive, complicated, results in loss of the adsorbent, and is energy-consuming. In addition, small and medium-sized enterprises cannot employ such expensive treatment.

All the above features indicate the necessity for finding alternative and more economic precursors from non-conventional resources to prepare activated carbon, namely, waste materials with little or no economic value. They often present a disposal problem, making them appropriate alternative materials to prepare activated carbons. In light of that, most of the current research is focused on the production of activated carbons from agricultural and wood waste due to some unquestionable advantages: this process results in the revalorization of waste, reduce the cost of its disposal, the obtained activated carbons have a lower cost since they are produced from low economic value precursors, they are obtained from renewable resources, and after their lifetime, the combustion of these activated carbons does not imply a direct increase of CO₂ accumulation in the atmosphere because this CO₂ has been previously captured during plant growth (Bedia et al. 2020).

A wide variety of activated carbons have been prepared from agricultural and wood wastes, *e.g.*, bagasse, banana pith, date pits, sago waste, silk cotton hull, maize cob, straw, rice husk, potato peels, porous beetroot, fruit stones, pinewood, sawdust, and bamboo, as well as from various city wastes and industrial by-products, *e.g.*, waste PET bottles, waste tires, refuse-derived fuel, sewage sludge, waste newspaper, waste carbon slurries and blast furnace slag (Yahya et al. 2015). Many of them have

been tested and proposed to remove heavy metals, dyes, and pesticides. As discussed in detail below, there are several reports on the production of activated carbons from hemp in the form of fibers, shives, stems, bast, and stalk. Fundamental research is currently very active concerning this topic since there is a demand for clean water using low-cost and efficient carbon-based technologies. Besides wastewater treatment, activated carbons are widely used in many other applications, including catalysis, mostly as supports of the active phases (Rey et al. 2016; Yang et al. 2017; Fang et al. 2018; Palomo et al. 2019; Mo et al. 2020) but also as bulk catalysts (Valero-Romero et al. 2019), and in electrochemical or energy storage applications such as supercapacitors (Abioye et al. 2015; Ibeh et al. 2019).

Yang et al. (2017) prepared three-dimensional heterogeneous hemp-derivate porous activated carbons employed as catalyst supports for direct deposition of vertical MnO₂ wires. The resulting composites were further used as catalysts for glycolysis of poly(ethylene terephthalate) with a high conversion yield of 98%. Most recently (Mo et al. 2020), the hemp-derived activated carbon was used to support zero-valent iron (ZVI@HAC) as a heterogeneous Fenton catalyst to treat pulping effluent. Under the optimal conditions (initial pH of 3.0, 35 mmol/L H₂O₂, and 3.0 g/L ZVI@HAC), the chemical oxygen demand removal rate reached 87.74%. Additionally, Zhang et al. (2020a) prepared Co/N doped hemp-derived highly porous carbon exhibiting excellent oxygen reduction reaction electrocatalytic performance with high half-wave potential (0.826 V), superior catalytic stability, and tolerance to methanol.

4.2 Carbonization of Hemp-Based Products

Lignocellulosic materials such as hemp represent suitable carbon precursors since they contain cellulose, hemicelluloses, and lignin which are carbon-rich components. Such heterogeneous hemp's chemical composition and complex structure affect the specific surface area, amount of surface oxygen groups, and morphology of resulting carbons.

Hemp-based carbon materials can be obtained by hemp thermal decomposition in an inert atmosphere, which undergoes the pyrolysis, involving hemp softening and releasing of volatile compounds, which contribute to significant weight loss, and carbonization, representing the conversion of depolymerized fiber structure into graphite-like layers through the re-polymerization (Kostić et al. 2019). On the other hand, activated carbons with large specific surface areas and well-developed internal pore structures can be produced using physical or chemical activation. The physical activation involves precursor carbonization at 600–900 °C in an inert atmosphere to produce carbonized material afterward activated using water steam, carbon dioxide, air, or their mixture (Hina et al. 2018). In the first step, heteroatoms are removed, and volatiles are released, resulting in high carbon content (the increase of the carbonization temperature increases carbon content) but with low porosity development (Bedia et al. 2020). The second step involves the selective removal of

the most reactive carbon atoms by controlled gasification reactions that generate the characteristic porosity of the activated carbons (Bedia et al. 2020).

Compared to physical activation, chemical activation is performed in a single thermal step, although it consists of three different stages. In the first stage, the precursor impregnation with an activating agent such as KOH, ZnCl₂, K₂CO₃, AlCl₃, Na₂HPO₄, or H₃PO₄ can be performed in contact with the aqueous solution of an activating agent or, simpler, by its physical mixing with an activating agent. The activation process mechanism, along with the activation parameters used (especially the mass ratio between the activating agent and the precursor), significantly influences the textural characteristics of the final activated carbon. The second step includes thermal treatment in an inert atmosphere at different temperatures depending on the chosen activating agent, whereby reactions of depolymerization, dehydration, and condensation take place, while the last stage involves washing to remove the remaining activating agents and reaction byproducts that occlude the newly formed porosity and drying. An initial carbonization step is usually needed when the NaOH or KOH are used as activating agents of “soft” carbon precursors. Otherwise, these strong bases can dissolve the precursor organic matter, making the subsequent activation impossible (Bedia et al. 2020). Compared to physically activated carbons, chemically activated carbons have higher surface areas and a higher tendency for adsorption; their pores are mainly micropores, while physically activated carbons have mainly mesopores.

In the research conducted by Williams and Red (2003, 2004), Rosas et al. (2009), Sun et al. (2013), and Zhang et al. (2017), detailed characterization of hemp-based carbons prepared by physical activation with steam and chemical activation with H₃PO₄ or KOH have been reported. Williams and Reed (2003) first studied the preparation of activated carbons by hemp fiber carbonization and physical activation with steam. The surface areas of such activated carbons increased with increasing activation temperature, whereby a maximum surface area of 900 m²/g was registered at 60 wt.% burn-off. The obtained activated carbons were mainly microporous. However, the mesoporosity of the carbons also increased with increasing burn-off. A year later, the same authors prepared hemp-based carbons with significantly higher surface areas (over 2000 m²/g) by carbonizing ZnCl₂ impregnated hemp fibers and concluded that increased surface areas were associated with a higher concentration of activating agent and lower pyrolysis temperature (Williams and Reed 2004). The carbonization process influenced the pore size characteristics of the obtained carbons but was mainly microporous in nature.

Later, Rosas et al. (2009) published a similar conclusion. They prepared hemp-based activated carbon fibers by chemical activation with H₃PO₄ at different carbonization temperatures and impregnation ratios. Carbons' characterization revealed that their surface characteristics were significantly influenced by the activation temperature and the impregnation ratio. An increase of either of these parameters produced a highly developed porous structure of the fibers.

Using an air-phosphoric acid activation method, mesoporous activated carbons using hemp stem as precursors were prepared by Sun et al. (2013). Data indicated that the concentration of H₃PO₄ solution significantly affected the pore structure and

adsorption property of the resulting activated carbon. The mesoporous activated carbon obtained with a 50% H_3PO_4 solution had a developed pore structure, a wider pore size distribution, and a maximum BET specific surface area of $1351 \text{ m}^2/\text{g}$.

Zhang et al. (2017) prepared and characterized high surface area activated carbons from hemp stems using the KOH activation protocol. They reported the involvement of methylene's substitution, scission, and oxidation reactions during the carbonization process, polycyclic reactions, reactions between carbon and KOH, and reactions between intermediate potassium oxide species and carbon during the activation treatment. These reactions play an important role in controlling the activated carbons' porosity and, consequently, their adsorption properties. Reported KOH activated carbons had high specific surface areas, well-developed pore structures, and microporous features.

Lupul et al. (2015a, b) and Liu et al. (2017) also showed that the carbon textural characteristics such as micropore volume, pore size distribution, surface area, and chemical properties depend on the carbonization and activation processes. These authors indicated that chemical activation had the advantage of highly effective and well-controlled porosity compared to physical activation.

4.3 Applications for Pollutant Removal

Literature data summarized in Table 7 demonstrate that non-conventional carbons obtained from hemp (in various forms: fibers, stems, shives, bast, and stalk) exhibited high biosorption capacities for various inorganic and organic pollutants such as heavy metal ions, ammonia nitrogen, pesticides, dyes, phenols, etc. The adsorption capacities of non-conventional carbons, including hemp-based carbons depending on the carbonization and activation process parameters (i.e., temperature, time, activation agent, and carbonized material/activation agent ratio) and treatments performed before or after carbonization. All mentioned variables contributed to obtaining hemp-based carbons with very different specific surface areas, microporous structures, a wide spectrum of surface functional groups, and hence to obtaining hemp-based carbons with very different specific surface areas and microporous structures wide spectrum of surface functional groups, and a degree of surface reactivity.

Vukčević and co-workers reported that hemp-based carbons (both non-activated and activated with KOH) from waste short hemp fibers were very efficient for the removal of lead ions (Vukčević et al. 2017) and pesticides such as nicosulfuron, carbofuran, atrazine, acetamiprid, and dimethoate (Vukčević et al. 2015), showing its competitiveness against commercial systems. The adsorption of lead depends on the chemical modifications (alkali and oxidative) performed before the fiber carbonization (Vukčević et al. 2017). A detailed sample characterization indicated that the lignin content and polymorphic transformation of cellulose I to cellulose II increased the specific surface area of microporous carbons, while the hemicellulose removal induced a more homogeneous distribution of active adsorption sites. Lead

Table 7 Adsorption capacities (q_{max} , mg/g) of hemp-based carbons, obtained by carbonization or carbonization and further activation, for various pollutants

Carbon precursor	Carbonization process parameters	Activation process parameters	Additional treatment	Experimental conditions (biosorbent dosage, time)	Adsorbate	q_{max} , mg/g	Reference
Hemp fibers	1000 °C, 30 min	/	/	0.1 g/25 mL, 24 h	Pb ²⁺	106.7	Vukčević et al. (2017)
						114.9–116.3	
						103.1–113.3	
Alkali treated hemp fibers	700 or 1000 °C, 30 min	Carbonized material/KOH ratio of 1/1 or 1/2, 900 °C, 30 min	/	0.2 g/50 mL, 3 h	Nicosulfuron	11.6–19.5	Vukčević et al. (2015)
Carbofuran					13.0–15.7		
Atrazine					14.5–38.4		
Oxidized hemp fibers	600 °C, 1 h	Carbonized material/KOH ratio of 1/3, 700 °C, 1 h	/	0.05 g/100 mL, 2–5 h	Acetamidrid	12.2–19.3	Lupul et al. (2015a)
					Dimethoate	11.8–47.0	
					Atrazine	437.0	
Hemp stems	600 °C, 1 h	Carbonized material/KOH ratio of 1/3, 700 °C, 1 h	/	0.05 g/100 mL, 2–5 h	Atrazine	167.0	Lupul et al. (2015a)
						317.0	
						466.0	

(continued)

Table 7 (continued)

Carbon precursor	Carbonization process parameters	Activation process parameters	Additional treatment	Experimental conditions (biosorbent dosage, time)	Adsorbate	q _{max} , mg/g	Reference
Hemp stems	500–700 °C, 2 h	Hemp stems pretreated with tetrabutyl orthotitanate, 75 °C, 5 h ^a	/	0.03 g/50 mL, 24 h	Ammonia nitrogen	99.3% ^b 99.7% ^b	Peng et al. (2019)
Hemp stem	550 °C, 2 h	Carbonized material/tetrabutyl titanate ratio of 1/40, 140 °C, 13 h ^a	/	0.1 g/100 mL, 30 min	Ammonia nitrogen	60.7% ^b	Peng et al. (2020)
		C ₃ N ₄ /TiO ₂ /hemp stem biochar carbon, 500 °C, 2 h, under nitrogen flow ^e	/				
Hemp stems	500–800 °C, 2 h	1 g hemp stem/2.5 mmol FeSO ₄ , 3 h	/	0.1 g/100 mL, ~23 h	C ⁶⁺	127.7	Yang et al. (2014)
Hemp bast	450 °C, 2 h	Hemp bast/2.5 mol/l H ₃ PO ₄ ratio of 1/50, 110 °C, 6 h	/	0.04 g/20 mL, N/A	Acid Blue 9	28.75	Yang et al. (2011)
Hemp shives	600 °C, 30 min	/	H ₂ SO ₄	0.02 g/20 mL, 24 h	Acid-extractable organics from the oil sands process affected water	0.08	Bhuijan et al. (2016)
Hemp stalk	160 °C, 1 h	CO ₂ , 300 °C	/	0.05 g/50 mL, 140 min	Reactive Orange 16	41.32	Rehman et al. (2017)
Hemp shives	700 °C, 1 h	Carbonized material/KOH ratio of 1/4, 850 °C, 30 min		0.01 g/20 mL, 6 h	2,4-dichlorophenoxyacetic acid	540.6	Doczekalska et al. (2018)
					4-chloro-2-methylphenoxyacetic acid	493.5	

Chipped hemp fiber	400–425 °C	Chipped hemp fiber /Fe ₂ O ₃ /FeSO ₄ ·7H ₂ O/ CaMg(CO ₃) ₂ ratio of 10/1/1/1			PO ₄ -P	97% ^f	Bolton et al. (2019)
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^a Obtained product is TiO₂/hemp stem biochar composite

^{b, c} The removal efficiency of ammonia by photocatalytic degradation of ammonia nitrogen from aqueous solution under: (^b) UV light and (^c) visible-light irradiation

^d Obtained product TiO₂-CuO/hemp stem biochar carbon composite

^e Obtained product is C₃N₄-TiO₂/hemp stem biochar carbon composite

^f The removal efficiency

adsorption experiments demonstrated that adsorption capacities are mainly influenced by the number of surface oxygen groups while the specific surface area played a secondary role. In fact, carboxylic anhydride groups can be hydrolyzed in an aqueous solution rendering two carboxyl groups that might behave as ion-exchange sites to retain Pb^{2+} . In another work (Vukčević et al. 2015), it was reported that the adsorption performances of hemp-based activated carbons for pesticides removal were attributed to the carbonization and activation temperature, as well as to the ratio of carbonized material/KOH, contributing to obtaining activated carbons with relatively high specific surface areas (from 518 m^2/g up to 2192 m^2/g), dominantly microporous structure (from 386 m^2/g to 2111 m^2/g) and different surface chemistry, especially amount of surface oxygen groups. In general, specific surface area and pore size distribution are dominant factors affecting the physical adsorption of nonpolar organic molecules, while adsorption of inorganic and polar organic compounds is also influenced by the adsorbent surface chemistry (Vukčević et al. 2015). The hemp-based activated carbons prepared by Vukčević and co-workers were used not only for environmental applications but also as a solid-phase sorbent for the pesticide analysis in water samples with recoveries comparable or even better than those obtained with commercial cartridges (Vukčević et al. 2012).

Similar to Vukčević et al. (2015), Lupul et al. (2015a) used hemp stem-based activated carbons having different surface chemistry to study the adsorption of pesticide atrazine. After the activation with KOH, stems were further treated with HNO_3 , gaseous NH_3 or heated under nitrogen flow to introduce the oxygen and nitrogen functionalities on the biosorbent surface. However, the presence of such functionalities was found to be undesirable for atrazine adsorption. Heat treatment in the inert atmosphere of activated carbon enhanced its hydrophobicity resulting in obtaining the most efficient biosorbent for atrazine ($q_{max} = 466$ mg/g). A detailed analysis of the activated carbons showed that the treatments performed after the activation resulted in a removal of carboxylic and lactone groups, a decrease in the content of the acidic groups, and an increase of hydroxyl and nitrogen groups. Lupul et al. (2015a) indicated that the adsorption mechanism involved the presence of π - π dispersive interactions between the atrazine π electron ring and the π electron of carbon graphene layers.

The adsorption of pesticides onto activated carbons obtained from hemp in the form of shives was studied by Doczekalska et al. (2018). The results demonstrated that the activated carbons were efficient biosorbents for 2,4-dichlorophenoxyacetic acid ($q_{max} = 540.6$ mg/g) and 4-chloro-2-methylphenoxyacetic acid ($q_{max} = 493.5$ mg/g) from aqueous solution.

Besides heavy metal ions and pesticides, the activated carbons were also used to remove the dyes from aqueous solutions. Yang et al. (2011) reported that the textural characteristics of activated carbons obtained from H_3PO_4 impregnated hemp bast were strongly dependent on the carbonization temperature, ranging from 400 to 600 °C. Such prepared activated carbons were then used as adsorbents for dye removal, whereby the highest adsorption capacity for Acid Blue 9 ($q_{max} = 28.75$ mg/g) was obtained with the material activated at 450 °C. The

authors concluded that hemp bast was a suitable low-cost byproduct that could be used as an adsorbent to produce activated carbon for dye removal, thus contributing to sustainable development in both hemp production and environmental protection. The study conducted by Rehman et al. (2017) also proved that the activated carbon (using CO₂ as activating agent) from hemp stalk could be successfully used for dye removal. The biosorption capacity of 41.32 mg/g for Reactive Orange 16 was reported.

Recently, hemp-based materials have been proposed to capture harmful gases such as CO₂ using adsorption-oriented processes. This technology has advantages over others, such as membrane filtration, as it has higher selectivity, lower energy consumption, and low-cost production. For example, Liu et al. (2017) proposed activated carbon from hemp shives for CO₂ adsorption. After the carbonization of hemp shives, carbons were activated by using CO₂ or ZnCl₂. The yield of the ZnCl₂ activated carbons, and their specific surface areas were higher than those observed for carbons activated with CO₂. During activation, ZnCl₂ acted as a template for the pore formation, and after the activation, all the activated carbons exhibited significant micropores with the surface area exceeding 1100 m²/g. The activated carbon derived from hemp shives exhibited larger micropore and mesopore volumes than retted hemp shives. The results of batch studies for CO₂ capture reported that the CO₂ adsorption capacities of carbons activated with ZnCl₂ were higher than those activated with CO₂, related to their higher surface areas and pore volume. An improvement in the CO₂ adsorption capacity of activated carbons derived from the retting process was observed and attributed to the introduction of surface functionality. Finally, Liu et al. (2017) concluded that hemp products can prepare porous carbons used as efficient adsorbents for CO₂ capture.

In the previously analyzed papers, hemp in different forms was carbonized; however, literature in which the non-cellulosic components of hemp (*i.e.*, hemicelluloses and lignin) were extracted and further carbonized (Wang et al. 2015; Martin-Martinez et al. 2017 Rowlandson et al. 2020).

Another study on the use of carbons for CO₂ and CH₄ storage has been published by Wang et al. (2015). Hemicellulose extracted from hemp stem was used to prepare well-shaped carbon spheres with a surface area of 2192 m²/g in two steps. Firstly, a pre-carbonization strategy was employed to keep activated carbon in perfectly spherical morphology. Secondly, low-temperature hydrothermal carbonization and KOH activation were performed. The data on characterization demonstrated that when KOH/carbon ratio increased, the values of surface area, micropore and mesopore volumes, and surface oxygen content also increased. Activated carbon exhibited excellent electrochemical performance due to abundant micropores and plentiful oxygen functionalities. All these characteristics favor the adsorption properties of the materials, which are used to sequester CO₂ and CH₄ at ambient pressure and 0 °C. The results demonstrated that activated carbons converted from inexpensive hemp stems could be potential materials for CO₂ and CH₄ storage (Wang et al. 2015).

Rowlandson et al. (2020) extracted lignin using an identical Organosolv isolation method but from hemp hurds. Thereafter, the authors concluded that the ratio of

aromatic monomers (syringyl/guaiacyl ratio) in lignin was linked to the polymer's thermal behavior. High syringyl/guaiacyl ratio samples produced an inferior char yield than low syringyl/guaiacyl ratio lignins. Moreover, they swelled during heating producing carbon foam. Additionally, high syringyl/guaiacyl ratio lignin possesses the excellent potential to produce high surface area activated carbons with hierarchical porosity; macropores resulted from the swelling, and activation with CO₂ introduced meso- and microporosity.

Despite the growing number of research studies and published papers, the literature review shows that the specific mechanisms of pollutant adsorption on these non-conventional hemp-based carbons are still unclear. Two main types of adsorption mechanisms are proposed, physisorption, *e.g.*, hydrophobic interactions and electrostatic attraction, and chemisorption, *e.g.*, surface complexation and ion-exchange. Heavy metal ion adsorption on a carbonized material surface is generally established through physisorption, *i.e.*, electrostatic attraction between metal ions and graphene layer's π electrons. However, the role of the chemisorption should not be neglected since the biosorbent surface functional groups such as oxygen groups (considered as Lewis base) can coordinate with electron-deficient metal ions (Lewis acid). In the case of the adsorption of organic molecules on carbonized materials, electrostatic and non-electrostatic interactions can occur. Such interactions strongly depend on the charge densities of both the carbon surface and the adsorbate molecule and the ionic strength of the solution. Keeping in mind that the so-called attractive non-electrostatic interactions include van der Waals forces, hydrophobic interactions, and hydrogen bonding, the surface chemistry of the carbon has a significant influence on adsorption properties. Aromatic compounds can also be physisorbed on carbon materials by dispersion interactions between the π electrons of the aromatic ring and graphene layers. The presence of aromatic rings increases the level of organic pollutant adsorption.

The effect of carbonization and activation process parameters on the hemp-based carbon-specific surface areas, microporous structures, surface functional groups, and hence adsorption of different pollutants was studied in the previous part. However, the setting of optimum adsorption conditions and the evaluation of the adsorption mechanism by studying the influence of other experimental conditions (*i.e.*, solution pH, initial pollutant concentration, sorbent dosage, temperature, and adsorption time), the isothermal and kinetic modeling, and the thermodynamic parameters, have been performed only in few papers.

Vukčević et al. (2017) considered three of the mentioned experimental parameters (*i.e.*, solution pH, initial ionic concentration, and temperature) and studied their effect on lead ion adsorption on the hemp-based carbons. The solution pH of 5.5 was chosen as optimal since the highest adsorption capacity was observed at this pH value. In contrast, the competition between the protons and Pb²⁺ for adsorption sites decreased, preventing ion precipitation. The authors used four isotherm models to establish the relation between Pb²⁺ concentration and its adsorption onto hemp-based carbons. The experimental isotherm data showed a rapid increase in the adsorption values, especially in the alkali-treated hemp precursor (with 17.5% NaOH for 45 min), mainly due to the polymorphic transformation from cellulose I

to more reactive cellulose II. The temperature was another experimental parameter that was varied during the adsorption experiments. A thermodynamic study indicated that lead adsorption onto hemp-based carbons was a spontaneous and complex endothermic process, suggesting the coexistence of physisorption and chemisorption mechanisms. It is worth mentioning that among the three ions (Pb^{2+} , Zn^{2+} , and Cd^{2+}) studied, Pb^{2+} is the most competitive due to its high ionic radius and thinner solvation layer.

In another study conducted by Vukčević et al. (2015), contact time (0–180 min) and initial pollutant concentration (10, 20, 25, 40, and 50 mg/L) were considered as experimental variables affecting the pesticide biosorption onto hemp-based activated carbons. In general, the increase in the initial pesticide concentration contributed to the increase of adsorbed pesticide amount and the time required for reaching the adsorption equilibrium. The equilibrium pesticide adsorption onto hemp-based sample carbonized at 700 °C and activated at 900 °C (KOH/ carbonized material ratio of 2/1) having the highest amount of CO_2 evolving groups was reached after 20 min, while in the case of samples carbonized at 1000 °C and activated at 900 °C (KOH/ carbonized material ratios of 1/1 and 2/1), the adsorption equilibrium was reached after 60 min. Concerning the initial pesticide concentration, all examined activated carbon fibers showed an efficiency of over 98% for pesticide removal, regardless of their initial concentration. Isotherm adsorption data of dimethoate and atrazine were better fitted to Freundlich adsorption isotherm, while for all other pesticides (*i.e.*, acetamiprid, nicosulfuron, and carbofuran), isotherm adsorption data fit better to the Langmuir equation.

In contrast to findings reported by Vukčević et al. (2015), Lupul et al. 2015a showed that the data of equilibrium atrazine adsorption was controlled by the intraparticle diffusion mechanism into micropores and a significant contribution of film diffusion, fitted better with Langmuir-Freundlich and Langmuir models than Freundlich model. The observed difference can be attributed to Lupul et al. (2015a) using different precursors (hemp steam), which were activated using other protocols and treated. The authors also studied the effect of contact time on atrazine adsorption and concluded that the carbon surface increased hydrophilicity led to a longer time to reach equilibrium. More precisely, the time needed to reach equilibrium increased as follows: activated carbon treated with N_2 or NH_3 (2 h), non-treated activated carbon (4 h), and activated carbon treated with HNO_3 (5 h).

As discussed previously, the influence of the initial pH of pesticide solution on the adsorption capacity of activated carbons was not considered. However, Doczekalska et al. (2018) pointed out that the adsorption of pesticides 2,4-dichlorophenoxyacetic acid and 4-chloro-2-methylphenoxyacetic acid onto activated carbons obtained from hemp was pH-dependent, *i.e.*, the removal of both adsorbates decreased significantly with the increase of the initial pH of the solution. Accordingly, a pH of 2 was chosen as optimal for the adsorption studies. In this case, the pesticide adsorption was better represented by the pseudo-second-order model (equilibriums were achieved after 60–120 min), while the equilibrium data followed the Langmuir isotherm model.

As in the case of pesticide and heavy metal ion adsorption, the dye adsorption onto activated carbons is affected by different experimental conditions. A complex study regarding the factors affecting the adsorption of Reactive Orange 16 onto hemp stalk physically activated carbon was conducted by Rehman et al. (2017). The authors found that the adsorption was strongly dependent on contact time, adsorbent dosage and particle size, initial dye concentration, temperature, and pH. The results revealed that the equilibrium time for adsorption was 140 min for an initial dye concentration of 50 mg/L and 0.05 g/50 mL adsorbent at natural pH, while the highest adsorption was observed at a solution pH of 2. Isotherm experimental data fitted well with both Langmuir and Dubinin-Radushkevich models confirming the dual behavior of hemp stalk physically activated carbon for Reactive Orange 16 adsorption. This behavior was further confirmed by a pseudo-second-order kinetic model in which not only chemisorption was a rate inhibiting step but also physisorption. Moreover, values of thermodynamics constants ($\Delta G^\circ > 0$, $\Delta S^\circ < 0$, and $\Delta H^\circ < 0$) confirmed the adsorption of Reactive Orange 16 as nonspontaneous and exothermic.

The adsorption of Acid Blue 9 onto activated carbon from hemp bast (Yang et al. 2011) was described by Langmuir isotherm, while the adsorption kinetics was well fitted by the intraparticle diffusion model. In other words, Acid Blue 9 on the prepared carbon fibers was monolayer adsorption due to its small pore size and narrow pore size distribution.

Based on the above description, it could be concluded that hemp in different forms (*i.e.*, fibers, stems, bast, stalk, and shives) is a suitable precursor for the production of activated carbons, which will be further used as adsorbents for the removal of different pollutants such as heavy metal ions, pesticides, dyes, etc., thus contributing for the implementation of sustainable development in both hemp production and environmental protection.

5 Conclusion

In the past two decades, many hemp-based materials in raw, modified, or carbon forms have been proposed for pollutant removal from aqueous solutions, and numerous results were obtained at the stage of the laboratory-scale study. Outstanding adsorption capacities for metals and pesticides have been reported, mainly for synthetic solutions. From a technological point of view, the process is simple to set up. However, its feasibility for real polycontaminated effluents at an industrial scale must be proven. Future research also needs to clarify the adsorption mechanisms representing essential knowledge for understanding the adsorption process. A majority of publications have focused on evaluating biosorption performance, and only a few of them aimed to understand the adsorption mechanisms better. Also, despite the number of publications, few studies in the literature contain a complete study comparing various materials. Thus, much work is necessary to understand the adsorption phenomenon using hemp-based materials.

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