Chapter 244

Bryophytes in removal of environmental contaminants: Review and bibliometric analysis

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ABSTRACT
Bryophytes, especially mosses, have received growing attention because of their environmental applications, such as biosorption and phytoremediation. In general, this group is known for its sensitivity to environmental changes and the presence of pollutants such as metals, metalloids, persistent organic pollutants (POP), polycyclic aromatic hydrocarbons (PAH), components that are harmful to the environment and human health. Considering that bryophytes are cosmopolitan plants, the development of approaches employing them has great potential for use in different locations around the world. Given this, the present review seeks to evaluate the main aspects related to the environmental application of bryophytes in the removal of contaminants through biosorption and phytoremediation. For this purpose, the VOSviewer software was used in the elaboration of bibliometric maps, using information obtained from the Web of Science platform. The search related to the application of mosses in phytoremediation found 174 publications, the search related to the application of mosses in biosorption obtained 140 results. Of this total, it was observed that most studies were developed from 2005 onwards for both research areas, 2020 being the year with the largest number of studies using bryophytes in phytoremediation (n = 17), thus demonstrating that use this group is in growing development and has valuable application potential in the fields of biosorption and phytoremediation.

Keywords: Mosses, Sorbent, Biomass, Bibliometric mapping.

1 INTRODUCTION

The environment is continuously exposed to various contaminants from natural and man-made sources. The discharge of these contaminants deriving from anthropic sources remains an undue trend in urbanization and industrialization processes in many regions of the world, so that the presence of these contaminants in the environment is associated with several negative effects on human health and ecosystems (ȘTEFĂNUȚ et al., 2019; WU et al., 2016). Thereby, awareness of this situation has driven changes in the way we manage resources, design and use technology, and make decisions in society (HADDAWAY et al., 2018).

Over the years, a continuous expansion of research aiming at new approaches and developments to ensure environmental decontamination has been observed. Although there are established physical and chemical methods for removing contaminants, biological methods are gaining strength as a reliable alternative as compared to classic technologies, which, in general, are more expensive and less ecologically appropriate (BRUM et al., 2012; HLIHOR et al., 2014).

In the development and production of biomaterials and biosorbents, bryophytes have shown high potential in the removal of contaminants. The term bryophytes, in general, is used to designate mosses (Bryophyta), liverworts (Marchantiophyta), and hornworts (Anthocerotophyta), plants that have a life cycle marked by alternating gametophytic (haploid) and sporophytic (diploid) generations, being the dominant gametophytic generation (VANDERPOORTEN & GOFFINET, 2009). In comparison with other groups of plants, bryophytes are small organisms that live in direct contact with the surrounding environment, have a poikilohydric characteristic that allows them to absorb elements along their entire surface (ARES et al., 2017; ZECHMEISTER et al., 2003).

Bryophytes are important members of several ecosystems and contribute to soil stability, preventing erosive events and contributing to the increase in the rate of water infiltration into the soil (VUKOJEVIC et al., 2005). Its application in biosorption and phytoremediation is related to the removal, especially, of heavy metals present in the air, soil, and water (HAYNES et al., 2019; SANDHI et al., 2017; SUZUKI et al., 2016).

The objective of this study is to review by bibliometric analysis, presenting the current knowledge on the application of bryophytes in the biosorption and phytoremediation of contaminants.

2 MATERIALS AND METHODS

Firstly, a literature review using the Web of Science platform was performed aiming at verifying the scenario of publications related to the study subject. The terms used in the searches were "moss AND biosorption" and "moss AND phytoremediation". The analyses of the obtained information included the number of publications per year, the countries in which the studies were published, and the authors who published the highest number of articles on each specific subject.

Subsequently, the research for the bibliometric review focused on the main environmental applications of bryophytes related to their use in phytoremediation and biosorption, general perspectives and main challenges, to address the most relevant topics in this context. Bibliometric analyzes were performed using the VOSviewer software (version 1.6.15), using the Web of Science database. This platform was selected because it is a database with quality control of research material, peer-reviewed, related to the subject of the study.

From the information accessed in the database, bibliometric mapping was performed in the VOSviewer software, considering records from all periods and applying a methodology similar to that recommended by DE SOUZA et al., (2019). The main steps in the VOSviewer software consisted of feeding it with the obtained database to create a map of co-occurrence terms based on text data, taking into account words present in the title and abstract fields. The terms were extracted using the "binary count" method, in which only the presence or absence of the terms matters, while the number of occurrences of the term in the document is not considered. The minimum number of occurrences of the term was defined as 10, a standard recommendation of the software.

Thereafter, the most relevant terms for the research topic were selected, excluding measurement units as well as repeated and irrelevant items. The VOSviewer software generates maps considering the number of items in groups, according to their links. So, from the original map, it is possible to generate other maps by selecting a term and highlighting their respective links.

In the network view map, items are represented by their labels and also by a circle. The size of an item's label and a circle is determined by the relevance of each item, that is, the greater the relevance of the item, the greater the label and item circle. The color of an item defines which grouping it belongs to, and the lines between them represent their links. Furthermore, the distance between two items indicates the strength of the relationship, i.e., the closer the items are the more related they are and vice versa (ECK & WALTMAN, 2019).

Finally, a literature review was carried out based on publications available on the Web of Science platform. This review was performed to better characterize the connections between the extracted terms, support the discussion of results and the composition of the text, assessing the main applications of bryophytes, and checking the perspectives for future research and developments in these areas of study.

3 RESULTS AND DISCUSSION

3.1 CURRENT SCENARIO ABOUT PUBLICATIONS AVAILABLE ON THE WEB OF SCIENCE PLATFORM

Based on the results obtained on the Web of Science platform with the search for the keywords "moss * AND phytoremediation", on February 17, 2021, for all available years (1945-2021), 174 publications were obtained. Of this total, 158 articles, 13 event articles, 11 reviews, and three early accesses. The first registered publication is from 1997, and since 2005 there has been an increase in publications, with 2020 being the year with the most records, 17 in total. The country with the largest number of publications is China, representing 32.8% of all publications related to the subject. Brazil has a total of seven publications on the subject, the first in 2005 and the others in 2014-2020, indicating that the development of this theme is recent in the country.

Among the authors with the most prominent number of publications are Wong, with 12 publications, followed by Wu, with eight publications. In this regard, many are in partnership with each other, with issues related to soil remediation by arbuscular mycorrhizal fungi in the removal of metals, especially Cd, Zn and As, and polycyclic aromatic hydrocarbons PAHs.

Searching for the keywords “moss * AND biosorption *”, considering all the years allowed by the platform (1945-2021), 140 results were obtained, of these 134 scientific articles, 9 publications of events, two letters, and one editorial material. The first year with a record of publication on the subject was 1995, in 2002 the number of publications on the topic increased, with 2005 being the year with the most records, 13 publications, while in the other years (2006-2020), the publications followed an average close to seven productions a year. The countries with the largest number of publications are Romania and Turkey, with 17 publications each, amounting together 24.3% of scientific productions regarding this approach.

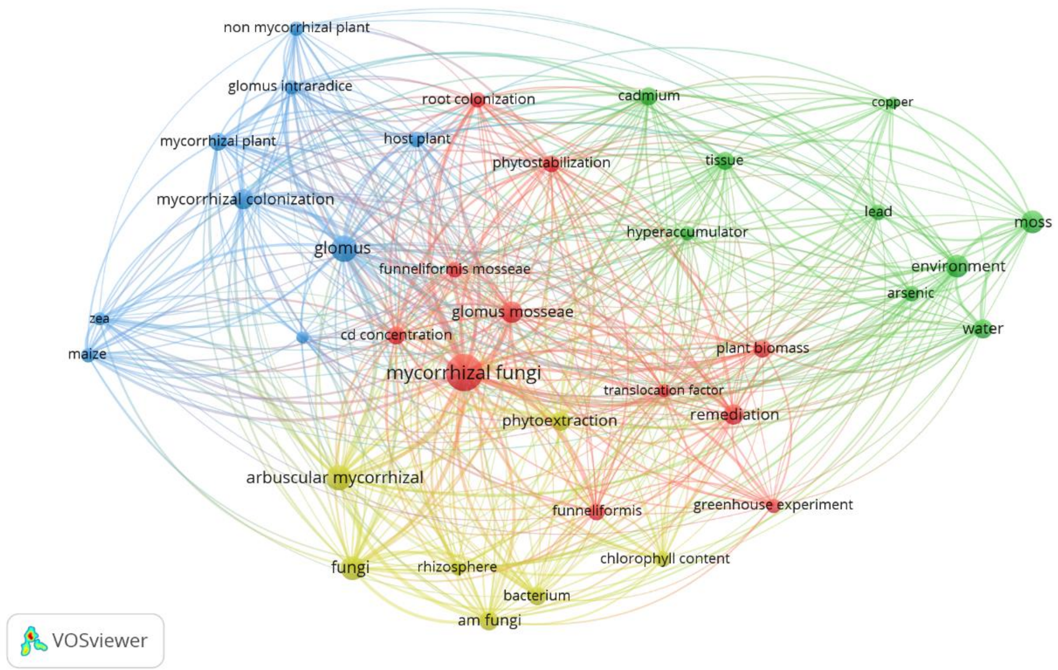
The authors with the largest number of publications are Macoveanu, M. and Bulgariu, L., with 13 and 9 publications, respectively. Both authors published the majority of their works together. The main approaches were associated with balance and kinetics of ion sorption metals by peat moss, in different pH, temperature and contact time ranges, analyzing the isothermal models of Freundlich, Langmuir, Tempkin and Dubinin-Radushkevich (BULGARIU et al., 2012a, 2009; KICSI et al., 2010a).

3.2 BIBLIOMETRIC MAPPING USING VOSVIEWER SOFTWARE

The search for the keywords “moss * AND phytoremediation” resulted in a total of 174 publications in the Web of Science database, on February 17, 2021, thus generating a network map shown in Figure 1.

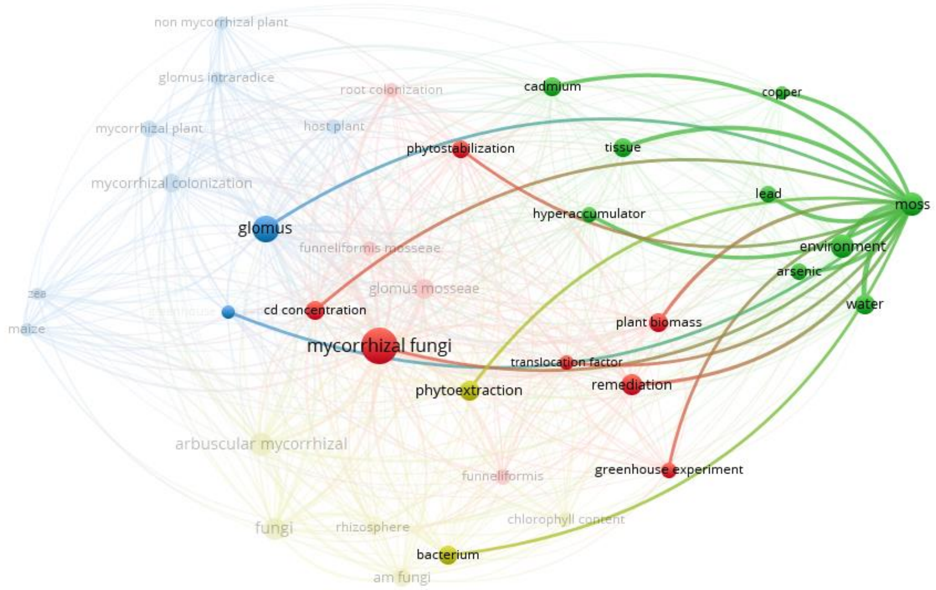
With the analysis of Figure 1, it is possible to observe that the software grouped the terms into four groups. Most of the terms have very close relevance, with the most relevant labels being mycorrhizal fungi and glomus. The green grouping comprises terms more related to the use of mosses in phytoremediation, especially in studies related to the remediation of metals such as cadmium, lead, copper, and arsenic, with water being the main remedied medium in the studies (PAPADIA et al. 2020). The blue and yellow clusters are mainly related to the use of fungi and bacteria in the remediation processes, especially associated with plant roots (LU et al. 2020). The red group has more terms associated with phytoremediation metabolisms, such as phytostabilization and phytoextraction, in addition to studies conducted from experiments in greenhouses and greenhouses using floristic biomass and addressing the ways of transporting compounds in the same (MATZEN et al. 2020).

Figure 1 - Network visualization map generated by the VOSviewer software from the search terms “moss AND phytoremediation” considering the Web of Science database. The colors represent the clusters of the extracted terms, grouped by the software according to their relationships.



By selecting the term “moss” (Figure 2), it is possible to visualize more clearly its direct connections with all items in the green group, mainly related to the remediation of metals in water (SANDHI et al. 2017), also its link with experiments in greenhouses and studies that associate the joint efficiency of mosses, mycorrhizal fungi, and bacteria (MUSHTAQ et al. 2020). In addition to studies on the metabolic functioning of remediation, phytostabilization, and phytoextraction, tissues and translocation factors in studies that evaluate how the compounds act in the plant after exposure (BELLINI et al. 2020).

Figure 2 - Selection of the term “moss” in the bibliometric map and the items related to the term generated in VOSviewer.

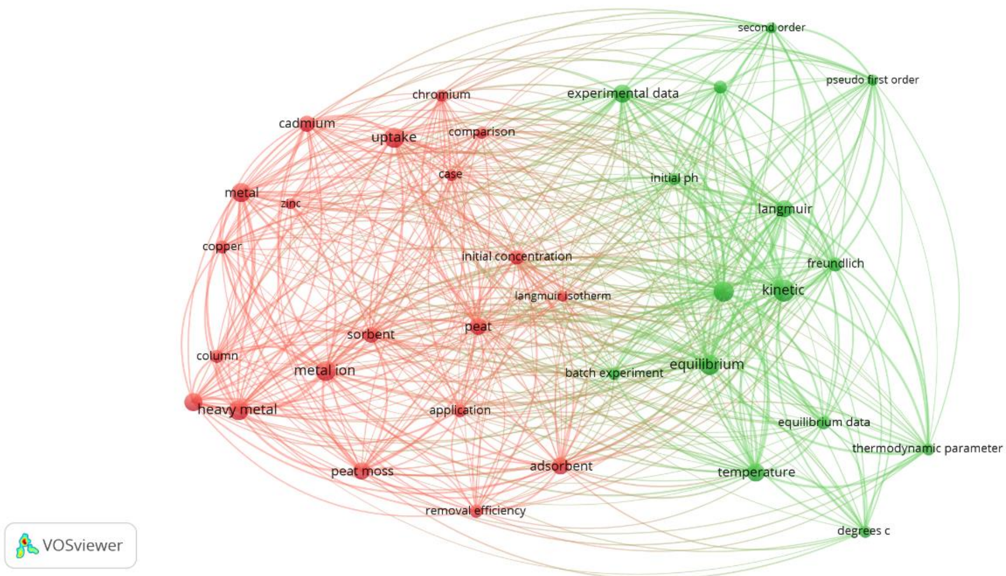


In Figure 3, a network map derived from the keywords “moss * AND biosorption” is presented. The search performed on February 17, 2021, and adopting the Web of Science database found a total of 140 publications.

Based on Figure 3, it is possible to distinguish two different clusters of terms. Most of them have very close relevance. Among the labels that presented the highest relevance heavy metal, equilibrium, kinetic, peat moss, and uptake. The green group comprises terms mainly associated with the absorption/adsorption models, such as dynamics and kinetics of accumulation, models (Langmuir), equilibrium and experimental data and batch experiments. The red group terms are more related to metals, such as absorption, maximum sorption capacity, zinc, copper, cadmium, and chromium, and the types of experiments and sorbents, comprising terms such as experimental results, peat moss, removal efficiency, and experiments in a column.

Considering the strong relationship between the terms of the different clusters grouped by the software, UCARLi et al., (2020), ŽUKAUSKAITĖ et al., (2019) and WANG et al., (2016) applied in their adsorption studies the adjustment of the results using the Langmuir isotherm model as well as obtained a better adjustment of the kinetic data through the pseudo-second order model. As adsorbents, UCARLI et al., (2020) and ŽUKAUSKAITĖ et al., (2019) tested species of peat moss, while WANG et al., (2016) used modified activated carbon with iron. The most prominent metals highlighted on the map of Figure 3 were tested in these studies. UCARLI et al., (2020) and WANG et al., (2016) carried out their experiments using batch systems, whereas ŽUKAUSKAITĖ et al., (2019) conducted experimental and modeling studies on a fixed-bed column filled with moss.

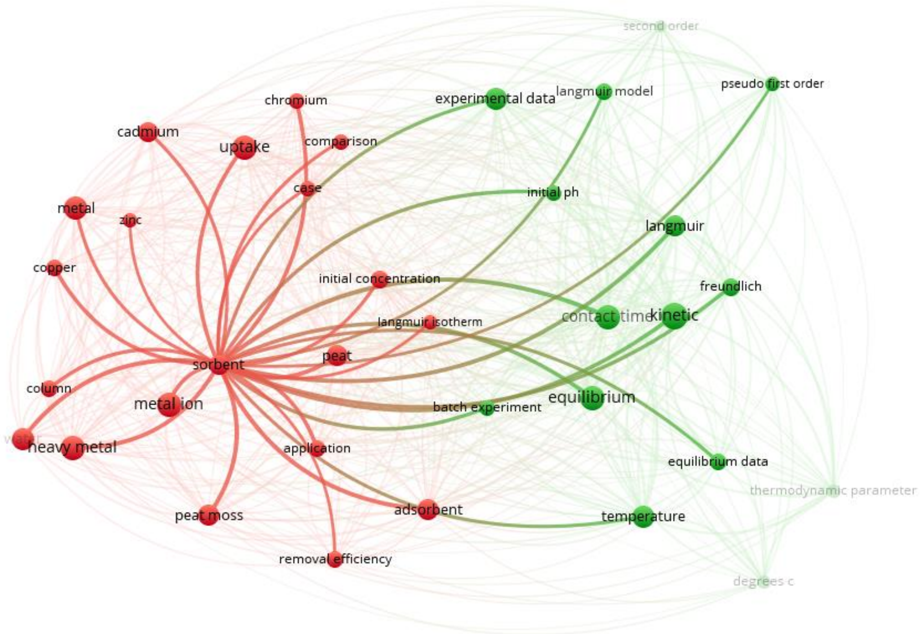
Figure 3 - Network visualization map generated by the VOSviewer software from the search terms “moss AND biosorption” considering the Web of Science database. The colors represent the clusters of the extracted terms, grouped by the software according to their relationships.



In the present research, another term selected was “sorbent” (Figure 4), initially presented in Figure 3. It was highlighted due to its importance related to the removal of contaminants, especially metallic ones. The most relevant and closest terms of the selected label were heavy metal, absorption, peat moss, balance, cadmium, and adsorbent.

In this context, most studies that use sorbents, present experiments performed on laboratory scale, under controlled and optimized conditions to define the best yields. Among the assays, the most frequently developed are in batch and continuous flow systems (LOW et al., 2001). Kicsi et al., (2010b) and BALAN et al., (2008, 2009) carried out batch adsorption experiments, using peat mosses belonging to the Sphagnum genus, in the removal of the metals zinc (Zn (II)), chromium (Cr (VI)), and Cd. The data of sorption balance were analyzed using the Freundlich and Langmuir isotherms, and the three studies showed removal reductions close to 100%, demonstrating the great potential of this group for the removal of metals present in water samples.

Figure 4 - Selection of the term “sorbent” in the bibliometric map and the items related to the term generated in VOSviewer.

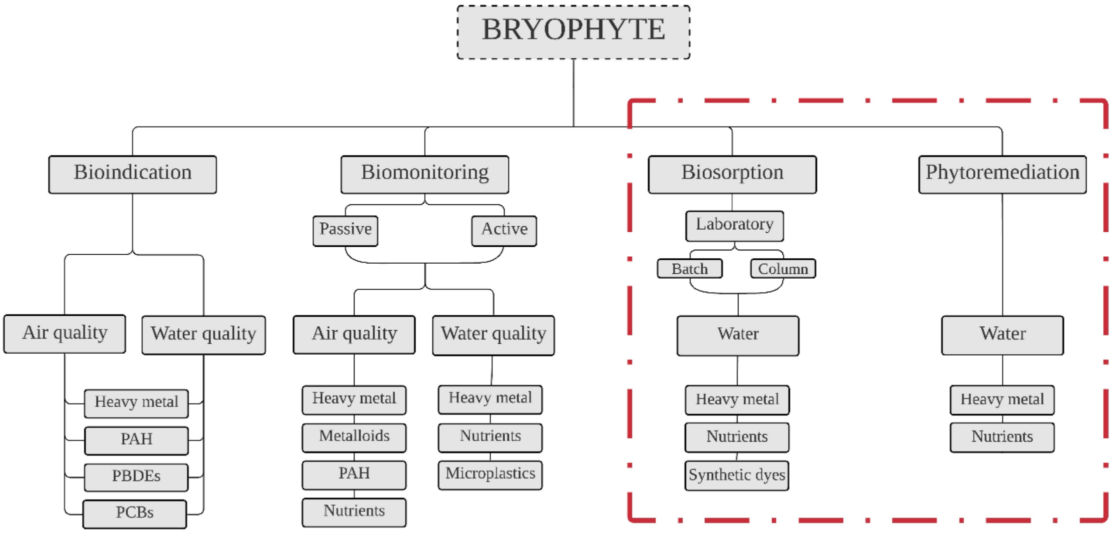


3.3 BIOSORPTION AND PHYTOREMEDIATION

The main environmental applicability of bryophytes, the use of these in biosorption and phytoremediation stand out. Thus, Figure 5 presents the main environmental applicability of bryophytes, with emphasis on the sectors mentioned above, considering the environments or systems, and contaminants in which they are most frequently studied.

Among the most prominent representatives in studies related to the environmental applicability of bryophytes, can be mentioned the division Bryophyta, represented by mosses, especially of the genera: Hypnum, Fontinalis, Sphagnum, Leptodictyum and Vesicularia.

Figure 5 - Applicability of bryophytes in bioindication, biomonitoring, biosorption, and phytoremediation, considering the main environments, systems and contaminants studied, with emphasis on employment in the sectors of biosorption and phytoremediation.



3.4 BIOSORPTION

Biosorption is a process in which biological materials are employed in mechanisms of adsorption, accumulation and enrichment aiming at the removal of contaminants, especially metals, in aqueous samples (HLIHOR et al., 2014; RIZZUTI et al., 2017). Therefore, the biosorption process is composed of electrostatic interactions and complex formations between ions and functional groups present in the material (SILVA, 2014).

In the adsorption treatment, which is a physical-chemical process, with the use of bryophytes, the main contaminants removed are dyes (PIPÍŠKA et al., 2018), metallic compounds (ŠUŇOVSKÁ et al., 2015), and nutrients (ZHANG et al., 2018). In this process, mass transfer and the retention of one or more constituents of a solute (adsorbate), present in a fluid step on the surface of a solid and porous phase (adsorbent), through physical and /or chemical interactions occur (ARAÚJO et al., 2018; NASCIMENTO et al., 2014).

As compared to other traditional methods of contaminants removal such as chemical precipitation (HU et al., 2020), ion exchange (IBRAHIM et al., 2020) and adsorption process with activated carbon (SOUZA et al., 2009), this treatment method may be considered more effective and economical. In general, it neither has no high energy requirements for production and maintenance nor produces toxic sludge during treatment (RIZZUTI et al., 2017; SILVA, 2014).

Table 1 presents a compilation of data considering studies that used mosses, peat mosses, algae, vascular plants and also physical-chemical methods to remove metals. From the exposure of the presented data, it is observed that the studies that used samples of mosses obtained higher sorption capacity of metals than other biosorbents. Also, they present similar or superior performance when compared to more traditional methods that are also frequently commercially used. For a complete understanding of the biosorption potential, the analysis of all the factors that influence the process is of great importance. These include the characteristics of the biosorbent, the physicochemical properties of the solution (temperature, pH, ionic strength), the initial concentrations of the solute and biomass in the solution (dosage of biosorbent/volume of solution), and also the speciation of metals (HLIHOR et al., 2014; NASCIMENTO et al., 2014; ŠUŇOVSKÁ et al., 2015).

Among the advantages that bryophytes present in comparison to other alternative biosorbents, their high surface/volume ratio and the presence of a thin cuticle are important characteristics that enhance their application as biosorbents and increase the ability to accumulate contaminants, especially metallic ones (BASILE et al., 2013).

Besides that, mosses have been used in biomonitoring related to surface water pollution as bioindicators and biomonitors (FAVAS et al., 2018), given their wide geographical distribution and characteristics that make them sensitive to a wide range of environmental pollutants. Therefore, moss biomass represents a potential biosorbent for removing contaminants present in water and effluent samples (MARTINS et al., 2014; OKOLI et al., 2017; ŠUŇOVSKÁ et al., 2015). Among the main applications of bryophytes as biosorbents, their use in laboratory experiments as well in batch (OZDES & DURAN, 2015) and in continuous flow (ŽUKAUSKAITĖ et al., 2019) tests, especially in water with mainly focused approaches, stands out in the use of dry biomass (OLU-OWOLABI et al., 2012; SARI et al., 2009).

In general, dry biomass can be more advantageous when compared to live biomass, as it does not suffer from the toxicity of contaminants, does neither require the addition of nutrients and nor the monitoring of chemical and biochemical demands for oxygen in solution (HLIHOR et al., 2014). Nevertheless, wet biomass can present higher removal efficiency rates in short exposure periods, because of the joint action of absorption and adsorption mechanisms, whereas dry biomass is only subjected to the adsorption process (SANDHI et al., 2017).

Table 1 - Comparison of different materials and methods used to remove metal contaminants present in water samples.

Material	**Type/Specie**	**Method**	**Contaminat**	**Inicial concentration**	**Sorption capacity**	**Removal efficiency**	**Reference**
Moss	*Pleurozium schreberi*	Biosorption	Cu	0.08 mmol/dm^3	0.030 mmol/g	37.2 %	Klos, 2018
Freshwater alga	*Spirogyra sp.*			0.017 mmol/dm^3	0.0031 mmol/g	18.23 %	
Moss	*Sphagnum sp.*	Biosorption	Cu	16 mg/L	6.83 mg/g	85.4 %	Ivanova *et al.*, 2016
				160 mg/L	30.16 mg/g	37.7 %	
Moss	*Polytrichum commune*			16 mg/L	6.33 mg/g	79.5 %	
				160 mg/L	21.2 mg/g	39 %	
Alga	*Parachlorella kessleri*			16 mg/L	7.42 mg/g	92.8 %	
				160 mg/L	46 mg/g	57.5 %	
Commercial cationic exchanger	Amberlite IR 120	Ion-Exchanger		16 mg/L	7.4 mg/g	96.1 %	
				160 mg/L	71 mg/g	95.3%	

Peat	Six peat types	Biosorption	Cr	-	-	92-100 %	Rizzuti *et al.*, 2017
Angiosperm	Mustard	Biosorption	Cd	-	33.56 mg/g	80 %	Bulgariu *et al.*, 2012b
Fungus	*Aspergillus niger*	Bioleaching	Cu, Ni, Co, Mn, Fe	-	-	97% (Cu) 98% (Ni) 86% (Co) 91% (Mn) 36% (Fe)	Mehta *et al.*, 2010
Brewers draff	-	Biosorption	Cr	-	132.6 mg/g	-	Šillerová *et al.*, 2013
Peat moss	-			-	154 mg/g	-	
Grape waste	-			-	428 mg/g	-	
Sawdust	-			-	46.7 mg/g	-	
Dolomite	-	Chemical precipitation	Fe, Cu	250 mg/L	-	98.4% (Fe) 3.18% (Cu)	Hu *et al.*, 2020
Zeolite	Bimetallic Oxide Nano Fe-Al	Co-precipitation	Cr	20 mg/L	44.74 mg/g	89.5 %	Kong *et al.*, 2020
Ion exchange membranes	PVDF/SnNPs	Phase Inversion	Cd, Cu, Ni, Pb, Zn	8.5 mg/L	-	70.7% (Cd) 92.8% (Cu) 63.9% (Ni) 93.9% (Pb) 82.3% (Zn)	Ibrahim *et al.*, 2020
Chelating resin	Iron(III) chelating resin	Selective removal	Fe	1248 ppb	1121.9 ppb/g	89.9%	Feng *et al.*, 1997
Activated carbon	Commercial activated granular carbon	Adsorption	Cr	5 mg/L	0.054 mg/g	97%	Souza *et al.*, 2009
				20 mg/L		99%	

3.5 PHYTOREMEDIATION

Phytoremediation refers to the use of plants in the remediation of contaminants through the removal, degradation, storage, or immobilization of contaminants from polluted environments, reducing their contents to safe levels to human health, and also to the ecosystem, acting in the improvement of physical, chemical and biological characteristics of these areas (BRUM et al., 2012; TAVARES, 2013).

Plants have an enormous capacity to absorb pollutants from the environment and carry out their detoxification by different mechanisms (ALI et al. 2013). Thus, in comparison with other remediation techniques, phytoremediation may be considered an ecological, more economical and sustainable method and, in general, does neither require large absorbents volumes nor the addition of chemicals (HETTICK et al. 2015; SINGH et al. 2015; HALDAR & GHOSH 2020; MARELLA et al. 2020).

In phytoremediation, vegetal species can act directly or indirectly to reduce and/or remove contaminants. In direct remediation, the compounds are absorbed and accumulated or metabolized in the tissues, through their mineralization. Indirectly, the plants extract contaminants from the environment, thus reducing the source of contamination or when the presence of plants provides a favorable environment for increasing microbial activity, which degrades the contaminant (TAVARES, 2013).

The absorption capacity of pollutants occurs through the mechanisms of phytoextraction (SHTANGEEVA et al. 2016), phytofiltration (SANDHI et al. 2017), phytotransformation (LI et al. 2016), phytovolatilization (LIMMER & BURKEN 2016), phytodegradation (AL-BALDAWI et al. 2015), phytostabilization (PEDRO et al. 2013) and phytostimulation (HAJABBASI et al. 2016). However, most of these mechanisms are studied and recognized mainly in other groups of non-bryophytic plants.

Therefore, to the present few studies have been developed with the application of bryophytes in phytoremediation. In general, phytoremediation is a process that involves the metabolism of the plant. Furthermore, is often also associated with interspecific relationships with other living beings, such as fungi, that assist in the removal of pollutants and other plants in which the phytoremediation species can settle.

Among the studies already developed, the main phytoremediated contaminants by bryophytes are metals (PAPADIA et al. 2020) and nutrients (HALLIN et al., 2015). The main species employed in this process are Warnstorfia fluitans (SANDHI et al., 2018), Sanionia uncinata (WOJTUŃ et al., 2019) and Leptodictyum riparium (BELLINI et al., 2020). Although phytoremediation may be considered a promising and versatile technique, which can be used in the remediation of contaminants present in the air, soil and water, when considering the use of bryophytes, the main application occurs in the aquatic environment (SUZUKI et al., 2016).

4 CONCLUSIONS AND PERSPECTIVES

The environmental applications of bryophytes represent an emerging and promising approach for the recovery of contaminated environments, especially related to their use in biosorption and phytoremediation. The group's cosmopolitan characteristic makes it possible to develop studies with different species of native bryophytes in each region, which can often be a determining factor in the performance during decontamination processes, also contributing to the conservation of the native flora, with a view to the possibility of cultivation of some studied species.

Conventional methods of decontamination present a series of disadvantages when compared to ecological ones, although they present similar efficiencies since they involve high operational costs for installation, execution, and maintenance. In addition to consuming more energy and often producing by-products that can be toxic to the environment and human health.

However, few studies have applied bryophytes in the biosorption or phytoremediation of systems at full scale and using real water matrices, most of which are carried out under laboratory conditions and using synthetic water matrices. This represents one of the biggest challenges related to the development and commercialization of biomaterials developed through the biomass of bryophytes.

For this, is important to evaluate in detail the remedied contaminants, the relationship between the removal of the contaminants and the physical-chemical parameters of the environment, if the application will be conducted in the forms of dry or wet biomass, which species will be used, if the treatment will be conducted only with a species of bryophyte or species in synergy, if it will occur with the addition of other chemical components that facilitate the decontamination process and also reflect on the possibility of reusing the biomass, the generation of contaminated residues and their final destination, facilitating cost calculations for each system.

Therefore, even with the increase in the number of publications in recent years, more research is still needed to develop and improve the applicability of bryophytes in the removal of contaminants, understanding the mechanisms that are involved in these processes, as well as the aspects necessary to optimize performance treatment, reducing environmental impacts, improving durability and reducing application and maintenance costs. The study of all these aspects is essential for the bryophytes to be more used in the removal of contaminants and to stimulate the development of efficient, sustainable bioproducts with commercial interest for the removal of contaminants from bryophytes.

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