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Review

Sustainable Application of Biosorption and Bioaccumulation of Persistent Pollutants in Wastewater Treatment: Current Practice

Cătălina Filote [1,2], Mihaela Roșca [1], Raluca Maria Hlihor [1,*], Petronela Cozma [1,2,*], Isabela Maria Simion [1], Maria Apostol [1] and Maria Gavrilescu [2,3]

[1] Department of Horticultural Technologies, Faculty of Horticulture, "Ion Ionescu de la Brad" Iasi University of Life Sciences, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania; catalina.filote@uaiasi.ro (C.F.); mihaelarosca@uaiasi.ro (M.R.); simion.i@uaiasi.ro (I.M.S.); mariabrinza2007@yahoo.com (M.A.)
[2] Department of Environmental Engineering and Management, "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof. D. Mangeron Blv., 700050 Iasi, Romania; mgav@tuiasi.ro
[3] Academy of Romanian Scientists, 3 Ilfov Street, 050094 Bucharest, Romania
* Correspondence: raluca.hlihor@uaiasi.ro (R.M.H.); petronela_cozma@ch.tuiasi.ro (P.C.)

Abstract: Persistent toxic substances including persistent organic pollutants and heavy metals have been released in high quantities in surface waters by industrial activities. Their presence in environmental compartments is causing harmful effects both on the environment and human health. It was shown that their removal from wastewaters using conventional methods and adsorbents is not always a sustainable process. In this circumstance, the use of microorganisms for pollutants uptake can be seen as being an environmentally-friendly and cost-effective strategy for the treatment of industrial effluents. However, in spite of their confirmed potential in the remediation of persistent pollutants, microorganisms are not yet applied at industrial scale. Thus, the current paper aims to synthesize and analyze the available data from literature to support the upscaling of microbial-based biosorption and bioaccumulation processes. The industrial sources of persistent pollutants, the microbial mechanisms for pollutant uptake and the significant results revealed so far in the scientific literature are identified and covered in this review. Moreover, the influence of different parameters affecting the performance of the discussed systems and also very important in designing of treatment processes are highly considered. The analysis performed in the paper offers an important perspective in making decisions for scaling-up and efficient operation, from the life cycle assessment point of view of wastewater microbial bioremediation. This is significant since the sustainability of the microbial-based remediation processes through standardized methodologies such as life cycle analysis (LCA), hasn't been analyzed yet in the scientific literature.

Keywords: heavy metals; microorganisms; persistent organic pollutants; removal mechanisms; process scale-up

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1. Introduction

In modern society, due to expansion of industrial and agricultural activities, an increasing number of toxic compounds are being released into the environment. Basically, natural ecosystems are not able to break down such pollutants and they are highly accumulated in air, water, soil and finally in the food chain [1,2]. Water has a very important role in the metabolism of living organisms while most biochemical reactions take place in its presence [3]. Today, water pollution is one of the main environmental problems facing humanity, especially as a result of the direct or indirect discharge into water bodies of contaminated effluents from various anthropogenic sources [2,4,5]. The quality of natural

water resources often needs to be improved to meet the qualitative requirements of consumers (such as drinking water, irrigation, industrial, for agro-zootechnical farms, etc.) due to the intensification and diversification of their pollution [6].

A huge concern is related to persistent, bioaccumulative, and toxic pollutants (PBTs). PBTs may be classified in inorganic or organic compounds or organometallic and other metallic complexes [7]. These environmental pollutants show high capacity and resistance against degradation under the action of abiotic and biotic factors, which gives them a high mobility into the environment. Their main classes are divided in persistent organic pollutants (POPs) (dioxins and furans, pesticides, chlorinated aromatic hydrocarbons, halogenated ethers, polychlorinated biphenyls – PCBs, polycyclic aromatic hydrocarbons – PAHs, perfluorinated detergents, polybrominated diphenyl ethers – PBDEs) and persistent inorganic pollutants (PIPs) (heavy metals – HMs such as lead, mercury, cadmium and chromium) [7,8]. Their persistence is mainly associated with a high (bio)accumulation potential and high toxicity for living organisms [9].

PBTs are accountable for long-transport distances, high stability and high persistence. For example, PCBs are still found in different environmental compartments including animal tissues even though they are banned or restricted in many countries since 1970s [7]. For example, Rigét et al. [10] studied the evolution trends of PCBs during 6 years' time in Arctic biota and observed a decrease in the annual mean concentrations per year. In the ArcRisk project, Carlsson et al. [11] investigated the levels of PCBs and other POPs of several Arctic food products from a food market located in Nuuk, Greenland. The highest PCB concentrations were detected in narwhal mattak (frozen skin and blubber) followed by seal meat and salmon species. The main dominant congeners of PCBs were associated with PCB-153, PCB-138, PCB-118 and PCB-101 [11]. In line with the above findings, mercury or other metals were also detected in different fish tissues. For example, Yi et al. [12] in line with other authors [13,14], observed that the sediment is the major reservoir for trace metal pollution playing an important role in HMs uptake by fish. Although large concentrations of HMs are released in water bodies, the detected concentrations of HMs (such as Cu, Zn, Pb, Cd, Hg, Cr and As) were highest in the sediments, intermediate in fish and lowest in the water. This is because HMs are compounds with low solubility in water, do not degrade in water, being absorbed and accumulated on the lower layers of sediments. Further, sediments are habitats and a source of food for benthic fauna. Thus, pollutants may pose direct or indirect toxic effects on aquatic flora and fauna [12].

As a consequence, the presence of toxic pollutants in environmental compartments is causing harmful effects both on the environment and human health. Due to their persistence, HMs and POPs end up bioaccumulating along the food chain [12,15,16], people getting exposed to these pollutants through inhalation, by ingesting contaminated water and food and by dermal contact, for example with consumer products (cosmetics, cleaning products, pesticides, etc.) [16,17]. Each pollutant is known to have unique features and physico-chemical properties which provide specific toxicological mechanisms of action to living organisms. Clofibric acid (CLA) for example, a compound used in pharmaceutics, is a common persistent pollutant in wastewaters, which can last up to several years in the aquatic environment and can affect the endocrine mechanisms of living organisms [18,19]. Exposure to POPs at high levels, may cause different health problems such as cardiovascular diseases, diabetes, endocrine disruption, birth defects, dysfunctional reproductive systems and cancers [8].

It is therefore evident that specific measures should be considered in order to prevent, reduce or eliminate these toxic pollutants from contaminated media. Given the increasing environmental concerns and legal constraints related to maximum acceptable concentrations of pollutants imposed on discharged effluents, new cost-effective alternative technologies should be developed. The conventional physical and chemical technologies (adsorption, absorption, ion-exchange, membrane processes, chemical precipitation) involve high energy consumption and high costs along with the possibility of toxic

wastes generation or incomplete removal of pollutants [1]. In this attempt, the use of biomass-based sorbents, for example marine macroalgae [20], agricultural waste [9], including microorganisms for pollutants uptake has been demonstrated as being an environmentally-friendly and cost-effective strategy for industrial effluents treatment. In spite of this, the bioremediation technology is not yet fully applied at large scale. New effort should be made to support microbial-based biosorption and bioaccumulation processes upscaling. It would be also very interesting for these methods to find some alternatives to enable recovery and reuse of compounds with commercial application from the resulted biomass [21]. Using environmentally friendly alternatives (innovative compounds, innovative industrial processes) or pollution prevention by eliminating toxic compounds at the source will remain always the most preferred practices to attend a sustainable industrial production. Examples of innovative compounds are the nanomaterials that are increasingly studied in the last years. Graphene oxide combined with 2-aminobenzothiazole (GO-ABT) was used to recover the rare earth elements found in low concentrations in aqueous solutions. GO-ABT composites have been proved to be a promising adsorbent due to its capability to retain 100% of Er(III) even after ten regeneration cycles [22].

Biosorption and bioaccumulation processes involve a biological material (biosorbent) and a liquid phase (water) which contains the dissolved contaminant to be treated. Biosorption is a passive process that uses dead biomass where the toxic substances are adsorbed on the surface of biomass being the first step of bioaccumulation. Instead, bioaccumulation which is an active process, uses only living organisms where the contaminants are transported to the cell and further accumulated inside the cell [21,23]. Usually, the living organisms are not suitable for treating highly toxic organic/inorganic contaminants because the uptake of contaminants in large amounts could affect the metabolism of the organism and death may occur. This inconvenience is overloaded by inactive biomass [24]. Furthermore, the presence of multiple inorganic and organic persistent pollutants in industrial effluents usually occurs and significantly affects the bioremediation process, including the viability of the microbial biomass [25–27]. Advantages of using dead biomass instead of living biomass are that nutrients and energy sources are not required, better sorption capacity is provided, the processes are rapid, no toxic effects caused by contaminants are involved and the recovery of contaminants is easier allowing regeneration of the biomass. Besides these advantages, the dead microbial biomass can be reused through desorption process [28,29]. Bioaccumulation is considered a more complex and expensive process compared to biosorption [1,21,23]. At the end of its life cycle, the living and dead biomass loaded with metals that are considered micronutrients for plant development, can be applied to soils through composting [30].

There are many review studies that approach the biosorption and bioaccumulation processes using microbial biomass, among which persistent pollutants such as heavy metals are extensively analyzed [4,23,31–34]. The distinct environmental behavior, structure and properties of persistent organic pollutants compared to heavy metals led to the evaluation of the potential of microorganisms to remove these pollutants from the environmental compartments, in different studies. For example, Torres et al. [35] discussed about the removal of heavy metals and organic compounds such as antibiotics and dyes, which in fact are not included in the list of persistent organic pollutants. Gaur et al. [36] in their paper focused on the application of biodegradation/bioremediation for removing of persistent and non-persistent pesticides, PCBs and PAHs (as persistent organic pollutants) and pharmaceutical and personal care products from wastewater. In another review the potential of cold-adapted microorganisms to remove the POPs are presented, being highlighted in particular the enzymes involved in adaptation to cold conditions [37].

To obtain a more thorough perspective on the available scientific literature in the topic of interest, we conducted an analysis of the published papers in the last ten years, based on PubMed database (Figure 1). In case of the microbial remediation of heavy metals from wastewaters, the key words used were "microorganism heavy metals biosorption". The obtained results showed 93 published articles. To identify the published articles

referring to POPs the search was performed using "microorganisms persistent organic pollutants (or each POPs name according to the Stockholm convention list) biodegradation" words. After a careful analysis, 167 articles were identified as being related to the keywords used.

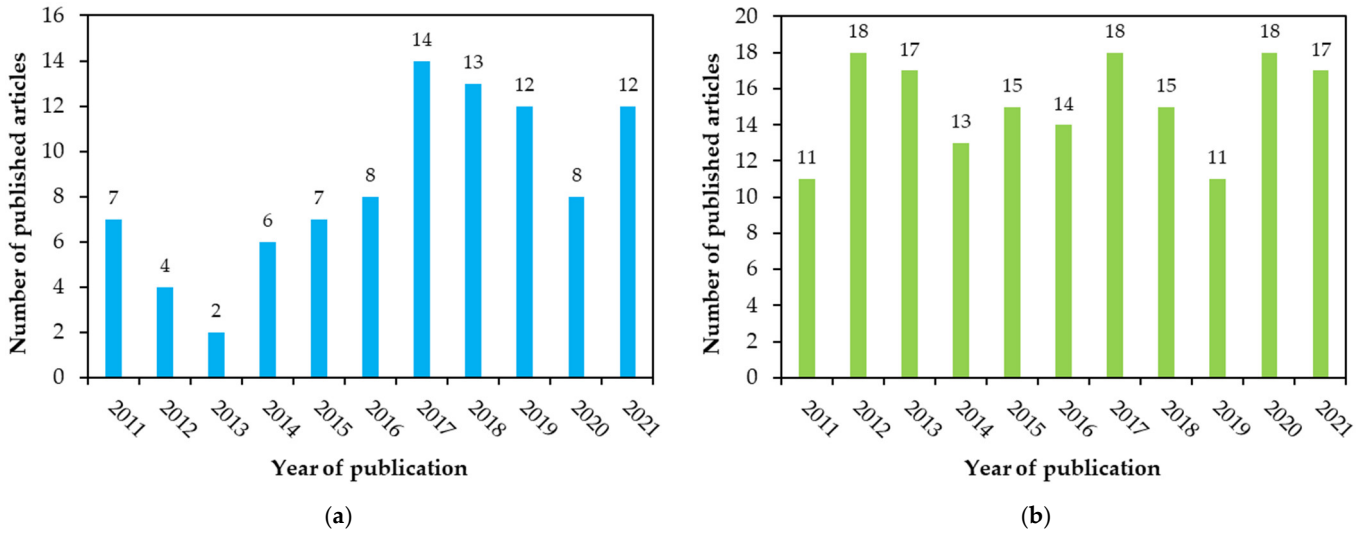

Figure 1. Number of published articles in international journals included in PubMed database: a summary of 10 years of publishing for (**a**) HMs biosorption by microorganisms and (**b**) POPs biodegradation by microorganisms.

In this framework and based on the available literature data, our paper reviews the main aspects related to: (i) the sources and the presence of HMs and POPs (listed in the Stockholm convention) in the environmental compartments; (ii) bioremediation of HMs and POPs contaminated waters by microorganisms: mechanisms, influencing factors and removal performance based on a large variety of microorganisms and under different operating conditions; (iii) key considerations and future perspectives for wastewater bioremediation scale-up considering life cycle assessment methodology. Knowing all of these aspects will enable controlling and performing of the process under industrial regime in order to be fully beneficial for the environment and society.

2. Sources of Persistent Pollutants and Contamination

2.1. Heavy Metals

Heavy metals (HMs) are naturally occurring constituents usually defined as elements with high atomic weight (greater than 40.04) and high density (larger than 4–5 g cm^{-3}) [38,39]. HMs are generally classified into four categories: toxic heavy metals (e.g., arsenic, cadmium, lead, mercury); essential nutrients for living organism (nickel, zinc, cobalt, copper, chromium, iron, selenium); precious metals (e.g., silver, gold, platinum) and radionuclides (e.g., uranium, thorium, tellurium, thallium, bismuth). The essential inorganic nutrients perform some metabolic functions for maintaining normal human health, but in large quantities they may pose acute and chronic effects [38,40]. Due to their high degree of toxicity, arsenic (As), lead (Pb), mercury (Hg) and cadmium (Cd) are listed by the United States Agency for Toxic Substances and Disease Registry (ATSDR), amongst the top ten hazardous substances that pose the greatest threat to human health [41].

Water is the most natural resource necessary to sustain food production and its contamination depleting the quality of life [3]. Volcanic eruptions, natural forest fires and bedrock weathering are the main natural sources of heavy metals that alter the water sources quality [39]. A high amount of pollutants are being released in water from different industrial activities, especially during the discharge of industrial, municipal and agricultural wastewaters and sewage into rivers [26]. Phosphate rock processing as well as

phosphate fertilizers use in agriculture are important pollution sources for surface waters [42]. So, the faulty control and management of industrial, municipal and agricultural effluents and sewage often can result in the transformation of receiving waters into inadequate resources for agricultural purposes (e.g., fishing and irrigation) [43]. HMs are found in different concentration in sewage sludge and industrial effluents that are finally discharged into water bodies. Once they have entered in the aquatic environment, HMs become available for accumulation in sediments and bioaccumulation in benthic organisms and finally in food chain. Since sediments are proper sink for heavy metals, their concentrations are higher in sediments and benthic fauna than in water [5,12]. For example, Algül and Beyhan [44] while investigating the quality of aquatic ecosystem in Lake Bafa (Turkey) found that the mean concentrations of heavy metals in the shallow sediments decreased in the following order: Fe > Mn > Ni > Cr > Zn > Cu > Co > Pb > Cd. They concluded that Cd, Cr, Cu, and particularly Ni may pose risks to the ecosystem of Lake Bafa and their high concentration are mainly caused by the use of pesticides and fertilizers, fuel combustion, releases of untreated wastewater from aquaculture facilities etc. [44]. Gabrielyan et al. [45] performed a research to investigate the distribution of heavy metals in the waters and sediments of the Voghji River (Armenia). It should be specified that Voghji River drains two mining regions. The investigation was based on data sets from period 2014–2016. The authors observed that Voghji River was most polluted with Mn, Co, Cu, Zn, Mo, Cd, and Pb, that were mainly released in water bodies from drainage water and wastewater of mining regions. Agoro et al. [26] provided a very complex study regarding the distribution of some selected heavy metals (Cd, Pb, Cu, Zn, and Fe) during the various stages of treatment in three sewage treatment plants in the Eastern Cape Province (South Africa). The operation of the three sewage treatment plants revealed a slight pollution. The majority of the five metals were detected in sewage sludge (Zn concentration was below the detection limit while Cu, Cd, and Fe were found in very low concentrations, below recommended limits). However, Cd was above the permissible level in all the samples considered (effluent, upstream and downstream samples).

HMs such as Hg, Pb, Cd, Cr and As even in low concentration may affect plants development by inhibiting root growth, synthesis of proteins and enzymes, damage to plasma membrane, and thus reducing food supplies by significantly decreasing of crops amount [46,47]. For example, Fargašová [48] used *Sinapis alba* L. as a model plant to test the toxicity of Cd, Cu, Pb, Se, Zn on its development. The phytotoxicity test was performed in hydroponic solutions at different metal concentrations. Copper and selenium affect in a lower extent the development of plant, while Pb reduced strongly enough photosynthetic pigments production. The metals accumulated into the roots and cotyledons decreased in the following order: Cd > Zn > Se > Pb > Cu [48].

In this regard, European Water Framework Directive (WFD) 2000/60/EC was implemented and Directive 2013/39/EC defined environmental quality standards (EQS) for priority substances (including metals) to minimize the discharge of toxic compounds into all ground and surface water within EU Member states [5].

According to the European Environment Agency (EEA), 38% of surface waters have a good chemical status, 46% do not have a good chemical status, while 16% provide an uncertain status in terms of water quality. A relatively low category of persistent pollutants is responsible for these results [49]. Of these, heavy metals, especially mercury, play an important role. Other metals with significant environmental impact are lead, nickel and cadmium.

Statistics on the contribution of various sectors of human activity to the contamination of aquatic environments with heavy metals in 2017 (Figure 2) showed that waste and wastewater management have a major contribution to water pollution with metals such as nickel (183 tons), lead (48.8 tons), arsenic (28.9 tons) and cadmium (8.55 tons), respectively, compared to other activities [50].

A significant source of heavy metals at international level is related to mining activities. Statistics from 2016 on the situation in Europe, indicated that 19% of the impact on

the environment is due to mining activities. Aquaculture also contributes to the impact of heavy metals on the aquatic environment, with a share of 14%. According to the European Environment Agency, Europe's energy-producing industry contributes with 6% to the impact of heavy metals on aquatic environments by exploiting the North Sea's oil resources and power plants on the continent [51].

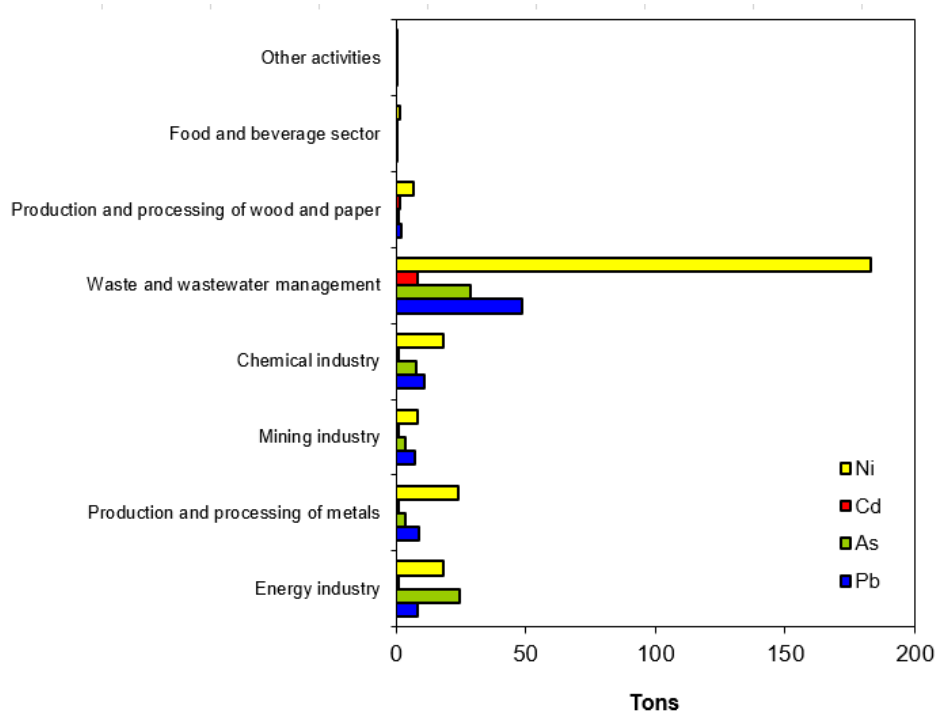

Figure 2. The contribution of various sectors of anthropogenic activity to the contamination of aquatic environments with heavy metals in 2017.

2.2. Persistent Organic Pollutants (POPs)

POPs are synthetic organic chemical compounds with a particular combination of physical and chemical properties that provide them some specific features. Thus, once they are released in the environment [16,17]:

- They persist and remain unchanged in the environment for very long periods of time (many years);
- They are widely distributed throughout the environment (in soil, water and, mostly, in air);
- They accumulate in the fatty tissue of living organisms and are detected in higher amounts at upper – trophic levels in the food chain;
- They are toxic to both humans and wildlife.

POPs are grouped in three categories [16,52,53]: (i) pesticides: aldrin, chlordane, lindane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene, pentachlorophenol; (ii) industrial chemicals: hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and (iii) unintended by-products: polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), PCBs, HCB, pentachlorobenzene, polyaromatic hydrocarbons (PAHs).

Due to their persistence in the environment, bioaccumulation/biomagnification in living organisms and associated hazard effects to biota, different global and regional conventions have been elaborated with the main purpose of eliminating or reducing emissions of POPs [10,54]. In this regard, the Stockholm Convention on Persistent Organic Pollutants initially addresses 12 priority POPs (the original 'dirty dozen') to be banned or used with restrictions, while the Protocol to the UN-ECE Convention on Long-range

Transboundary Air Pollution (UN-ECE LRTAP) covers the Stockholm Convention POPs and other four POPs [10]. The original 'dirty dozen' included organochlorine insecticides, PCBs, PCDFs and HCB. In present, other 16 new POPs are ratified by Stockholm Convention which include some non-chlorinated compounds such as perfluorinated detergents and polybrominated diphenyl ethers – PBDEs [55]. For complete details please see the list on priority POPs at [56] and [57].

There are many pathways to release POPs into the environment. First of all, POPs such as pesticides are used in agriculture being released as a result of plant protection treatments especially from their use, transport, storage and disposal [58]. Agriculture soil is the main source of soil pollution where POPs may enter through intentional discharges, unintentional spillages or deposition from air. Plant foliage uptake of POPs from air makes it possible their transfer to plant, and subsequently to food or may remain in soil where other possibilities can occur: re-emission, surface and subsurface flow, leaching in ground-water or degradation in soil [59]. Through re-emission, agriculture soils became a source of POPs in atmosphere [60]. Since POPs are considered lipophilic compounds they are not very soluble in water, meaning that the degree of POPs transfer to water may be relatively low. A more reliable process could imply the transport of POPs from soil to surface or ground water especially in intense rainy periods [60]. However, the majority of POPs are directly or indirectly emitted in air from different sources (waste incineration, fuel combustion, forest fires, furnace plants, power and heating stations, chemical synthesis of chlorinated substances, volatilization from water surfaces and soil, etc.) [58,59]. Overall, deep ocean, deep soil and sediments are known to be the final sinks for POPs [61].

At European level, according to the European Pollutant Release and Transfer Register, between 2015 and 2017 period, different quantities of pesticides and industrial organic pollutants belonging to the POPs category were released into EU surface waters. These pollutants mainly arise from economic activities, waste and wastewater management, chemical industry, energy sector and production and processing of wood and paper. Pesticides such as aldrin, dieldrin and endosulfan and industrial chemicals such as hexachlorobutadiene, pentachlorophenol and bromodiphenyl ethers were the main categories of POPs released into surface waters. As can be seen from Figures 3 and 4, industrial chemicals and by-products compounds are released in larger quantities in surface waters compared to pesticides [50].

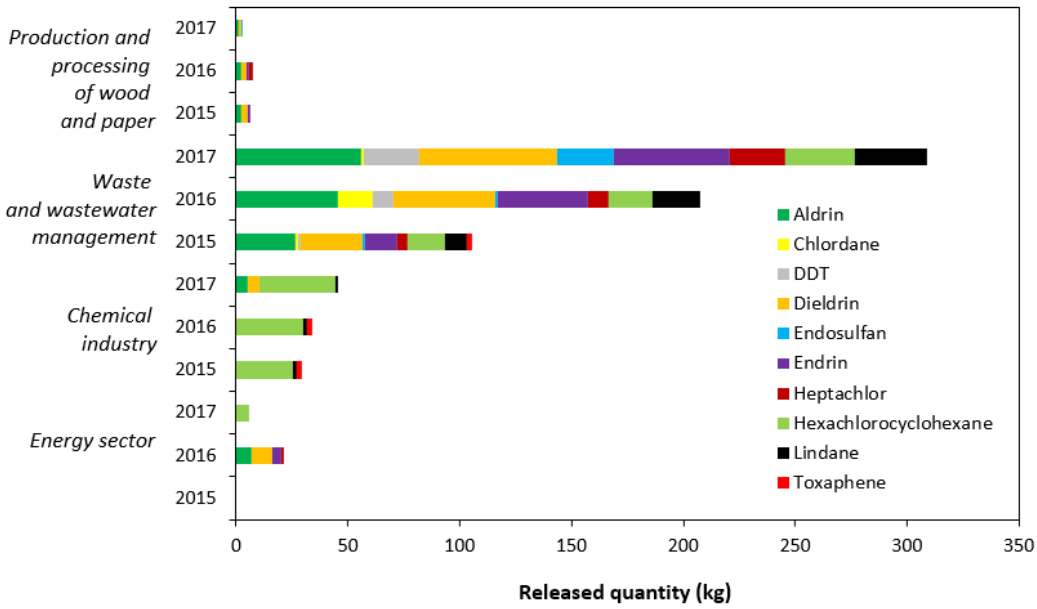

Figure 3. Pesticide emissions from various industrial activities in Europe's surface waters in the period 2015–2017.

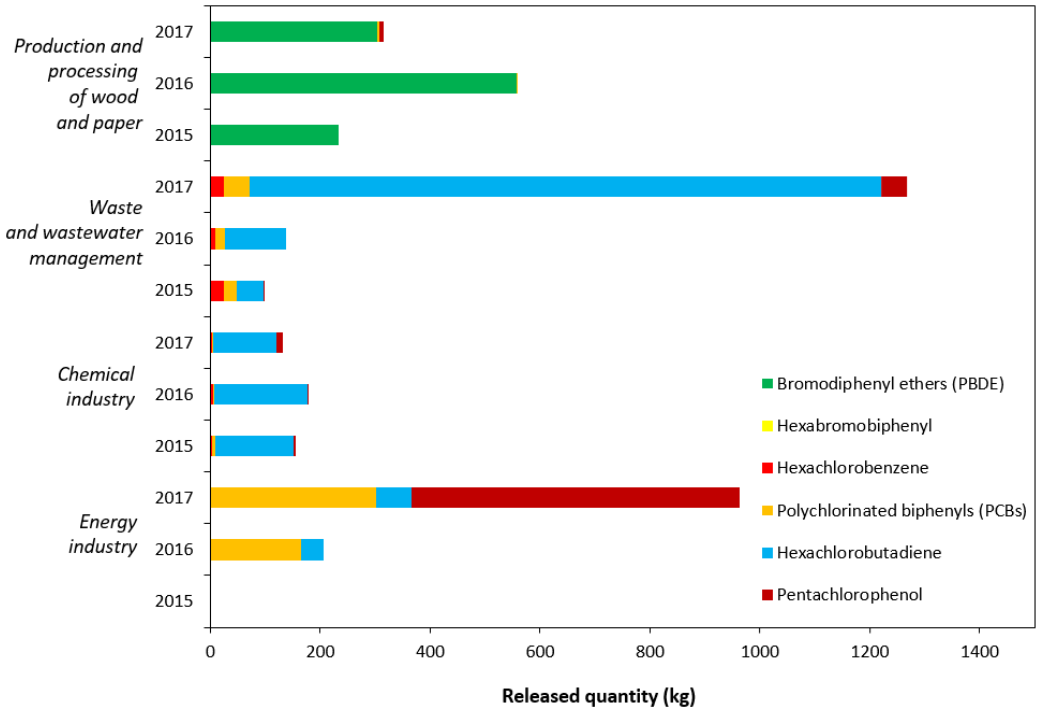

Figure 4. Emissions of industrial chemicals and by-products from various industrial activities in Europe's surface waters in the period 2015–2017.

2.3. Transport and Routes of Persistent Pollutants in the Environment

The release of pollutants into various environmental compartments (surface water, soil, groundwater and air) will lead to the subsequent transport of them from the point of emission to other components of the ecosystem, even in most isolated place on Earth like Artic Pole. As a consequence, the degree of pollutants accumulation will contribute to the exposure assessment of the population or flora and fauna existing in these compartments [62]. More precisely, persistent pollutants have the ability to enter and migrate along the food chain and increase their concentrations and retention times by a series of mechanisms denoted as biomagnification (or indirect bioaccumulation). For example, POPs are hydrophobic compounds with a high solubility in fats, thus accumulating in the adipose tissues of living organisms [63]. Heavy metals are elements that do bioaccumulate in living organisms causing changes at the cellular level [38]. These aspects attracted the attention of researchers to identify the transport routes and mechanism of pollutants between the environmental components and thus establish their cycle in the environment [19,20] (Figure 5).

3. Bioremediation of Heavy Metals Contaminated Wastewaters by Microorganisms

3.1. Mechanisms of Heavy Metals Removal by Microorganisms

Although they have different advantages and disadvantages, most studies indicate a higher level of removal performance for heavy metals through the biosorption process, compared with bioaccumulation [31]. Biosorption has been shown to be generally a rapid process that takes place in a few hours, while the process of bioaccumulation could last from several days to several weeks. Also, performing both processes under the same operating conditions indicated a higher remediation capacity in the case of biosorption [34].

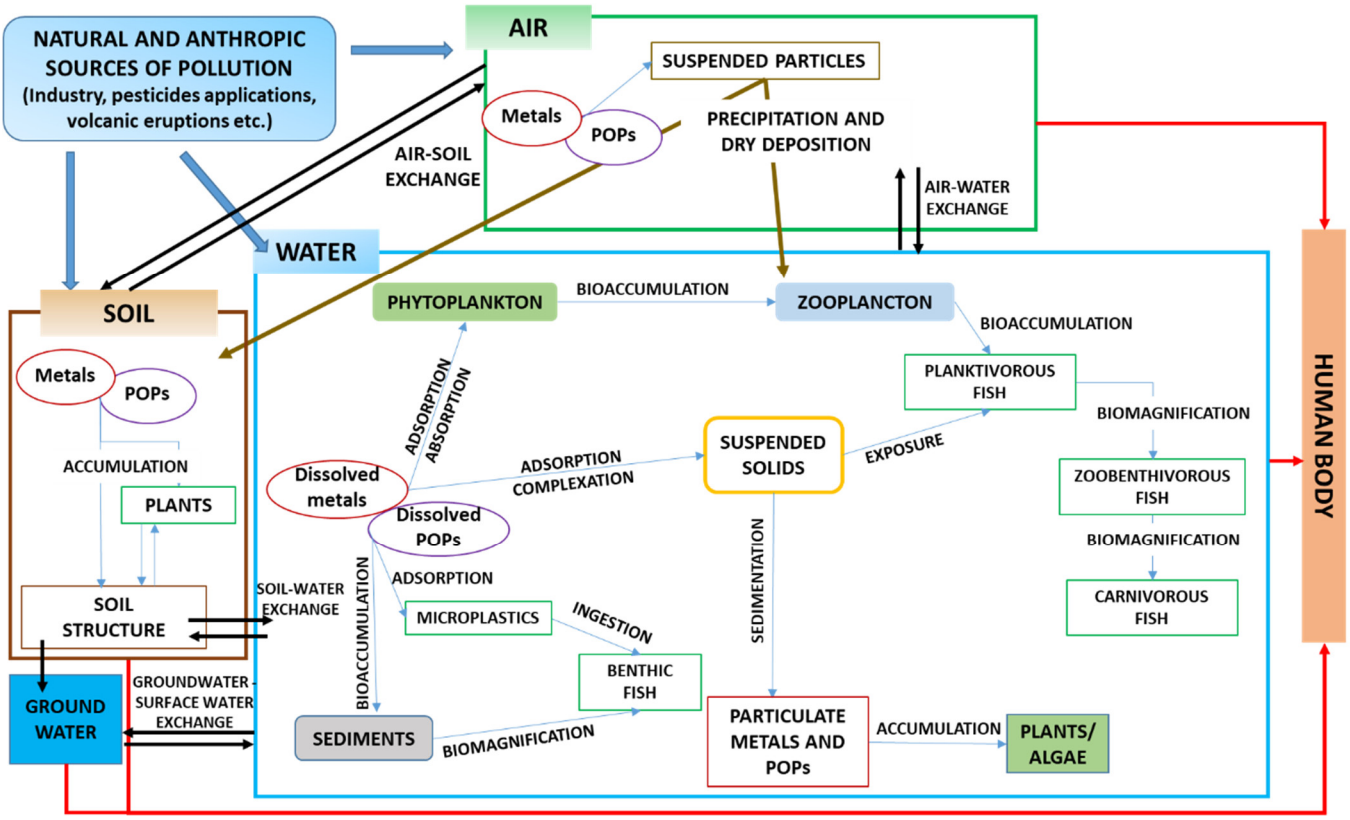

Figure 5. Transport and routes of persistent pollutants in the environment.

To achieve the maximum performance by microorganisms in the removal of heavy metals through the biosorption and bioaccumulation processes there are a number of important aspects to be attained. For example, certain metals such as cobalt, copper, manganese, iron and zinc [33,64] have a role in the proper functioning of cellular microbial metabolism, while others such as mercury, cadmium and lead have no role in the proper conduct of microbial processes [64,65].

The development of microorganisms is achieved through the lag, exponential, stationary and declining phases [66]. The lag phase is the period of adaptation of viable microorganisms to new environmental conditions or external factors. At this stage, the cell adapts to external influence through the formation of growth enzymes and other intermediates with a role in cell development. Usually, as the concentration of the metal to which the microorganism is exposed increases, the lag phase increases, and the maximum tolerance index in the stationary growth phase decreases [67].

The process of bioaccumulation of heavy metals by microorganisms involves two main stages, the first being biosorption at the cell wall, and the second being the incorporation of the pollutant into intracellular structures by biotransformation and metabolic pathways based on the use of enzymes and the ATP transport system.

Biosorption takes place through the formation of extracellular bonds, a process that takes place very quickly. Therefore, the second stage is achieved by slow-evolving metabolic processes that take place by transporting metal ions from the membrane to the intracellular structures and forming bonds with them. Thus, the chemical structure of the cell wall plays an important role in the biosorption mechanism, with the specific functional groups depending on the type of microorganism used [31].

Biotransformation consists of reduction, oxidation or alkylation processes that have an important role in determining the creation of metal species with low toxic effect. Bioprecipitation is another process with important function by producing proteins such as metallothioneins and phytochelatins, which form complexes with metals [31]. Studies to date show that the main mechanism involved in the biosorption of a metal is ion exchange.

Other elements and processes involved are van der Waals forces and complexation. Also, other mechanisms that can occur in both biosorption and bioaccumulation processes are associated with metal reduction, proton release, biomethylation, and chelation by ionic and covalent interaction [32,68].

The response mechanism of the microorganism to the pollutant consists first in the generation of extracellular compounds with a role in metal adsorption and precipitation, and in the second stage the binding of metal ions to thiol-containing metabolites takes place, with the formation of complexes stored in vacuoles or other compartments from the cell [67]. Proteins and peptides such as metallothionein mediate hormones and redox signaling molecules in the metabolic responses of microorganisms in contact with heavy metals [69]. Glutathione (GSH), a sulfur-containing compound, also plays a role in the detoxification process [67].

The remediation of wastewaters loaded with heavy metals is usually ensured by the following main microbial mechanisms [4,31,70] (Figure 6):

- bioaccumulation (I),
- surface complexation (II),
- bioprecipitation (III),
- ion exchange (IV),
- electrostatic interactions (V) and
- cell surface adsorption (VI).

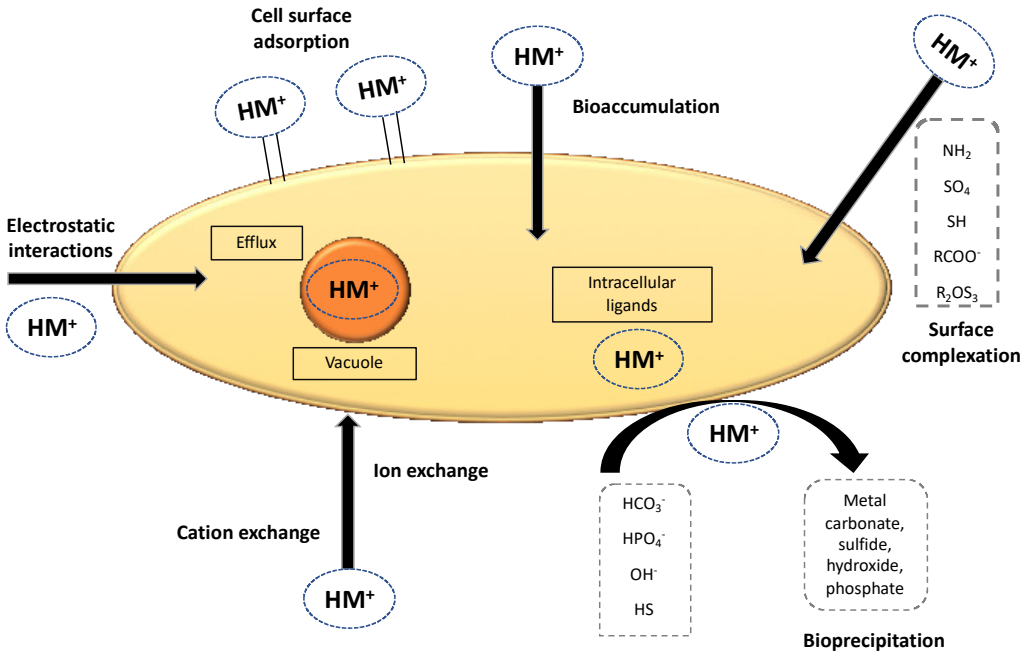

Figure 6. HMs removal strategy followed by microorganisms: the bioremediation mechanisms followed during the interaction between microorganism cell and HMs.

Very high potential for bioaccumulation or resistance to heavy metals has generally been identified in the case of microorganisms found in natural areas with extreme conditions or in the case of those naturally growing in contaminated sites. For example, a minimum inhibitory concentration of 4000 mg/L of cadmium was determined for *Paecilomyces* fungi specie. Also, minimum inhibitory concentration of 2000 mg/L was calculated in the case of *Aspergillus versicolor* and *Terichoderma* sp., while a value of 1000 mg/L of cadmium was identified for fungi species *Microsporum* sp., *Cladosporium* sp. and *Aspergillus fumigates* [71].

On the other hand, at concentrations of 20 mg Cd(II)/L, and 10–20 mg Pb(II)/L, respectively, the amount of chlorophyll decreased in the case of the cyanobacterium *Microcystis aeruginosa* [72]. Inhibition of chlorophyll synthesis of microalgae following exposure

to different concentrations of zinc has been demonstrated for many species, including those of the genera *Chlorella* and *Scenedesmus* [73].

Rhodococcus erythropolis isolated from a mining industry wastewater showed a tolerance to heavy metals in the range of 1–5 mg/L for Pb(II), 1–50 mg/L for Cu(II), 1–60 mg/L for Cr(VI), 1–80 mg/L for Zn(II) and 1–70 mg/L for As(V), respectively [74]. A new bacterium, *Halomonas* sp., isolated from effluents of the electronics industry, has demonstrated the ability to remove Cd(II) concentrations of up to 100 mg/L [75].

Extremophilic bacteria and organisms generally have very well-developed mechanisms for removing and reducing heavy metals, as they depend on them to survive. Such bacteria have been used, for example, to remove Cd(II) ions. At a preliminary study level, the bacterium *Brevundimonas* sp. ZF12 generated a removal efficiency of 45%, while a higher value was recorded for *Enterobacter* sp. ZF08, *Bacillus* sp. ZF10, *Shewanella* sp. ZF13, *Rothia* sp. ZF11, and respectively *Rhodococcus* sp. ZF05 [76]. Cr(VI) was removed after 72 h in a proportion of 74.2% by using the bacterium *Oceanobacillus* sp. W4, a bacterium isolated from soils polluted with this ion [77].

Trichoderma sp. is one of the fungal species with high tolerance to cadmium ions, resisting concentrations of up to 1000 mg/L [71]. However, certain differences were noticed in this interval in the influence of the evolution of fungal crops. Thus, in the case of *T. simmonsii*, increasing the Cd(II) concentration up to 125 g/L determined a fungal growth increase of 46.1%, and a decrease in the range of 125–500 mg/L [78]. Out of 41 species of filamentous fungi, isolated from the sediments of a river in Malaysia, only the specie *Aspergillus niger* was able to survive in cultivation conditions that include a Pb(II) concentration of 5000 mg/L. At the same time, in the same study, tolerance of up to 1000 mg/L of Cu(II) was reported for the species *Penicillium simplicissimum* [79]. The development of *Phanerochaete chrysosporium* species was inhibited by Cr(VI) concentrations higher than 10 mg/L, the bioaccumulation efficiency being reduced up to 23.82% [80]. *Penicillium chrysogenum* also showed a higher resistance to chromium, for concentrations up to 800 μg/mL, compared to *Aspergillus niger* [81]. Tolerance at concentrations of 1200 mg/L were detected in the case of *Aspergillus terreus* and 1000 mg/L in *Penicillium* sp., *Aspergillus lentulus* and *Fusarium solani* [82]. For the species *Aspergillus flavus*, contact with Hg(II) ions slows the development of mycelium, but a tolerance to concentrations of up to 100 mg/L of Hg(II) has been detected [66].

Remediation of metal ions can be achieved by microorganisms and biosurfactants such as rhamnolipids, compounds that achieve metal complexation [83]. Also, the response of microorganisms can be manifested by reducing the amount of extracellular solution absorbed, as well as by increasing the amount of metal removed from the intracellular environment [71]. Due to the high toxicity of Cr(VI), which once released in the intracellular environment is transformed into the Cr(V) radical which has a high instability and causes the appearance of reactive oxygen species (ROS)—generating further DNA degradation—microorganisms have adapted to extracellular reduction of Cr(VI) to Cr(III) form [84].

To reduce the mobility of heavy metals in wastewater, changing the oxidation state of the metal is often necessary through physical and/or chemical processes to obtain fewer toxic forms of the pollutant and more soluble or easy to remove. Microorganisms also have the ability to reduce the ionic forms of metals. Thus, they become easier to integrate into the cellular structures of microorganism. *Geobacter* species can transform U(VI) into the less soluble U(IV) form [69]. Also, the Cr(VI) species is usually reduced to the less toxic form Cr(III). In comparison with the conventional methods for reducing Cr(VI), that require a high amount of chemicals and a high level of energy, the use of microorganisms is considered to be less expensive and more sustainable. Also, in some cases, removal may be more effective in multi-metallic solutions [85]. Results of different studies have shown that for the reduction of Cr(VI) the optimal pH has a value of 7–8 [86]. Cr(III) has a slower diffusion across the cell membrane than Cr(VI), but certain complexes of Cr(V) and Cr(III) ions can penetrate more easily into the intracellular environment and cause cell damage.

Cr(V) species can occur by reduction of Cr(VI) ions the activity of microbial compounds such as cysteine, glutathione, riboflavin or ascorbic acid and is extremely toxic. Cr(V) causes DNA damage and mutations in bacterial chromosomes [87]. To determine the mechanism involved in the process of removal of Cr(VI) by the bacterium *Oceanobacillus* sp. W4, the role of electron donors acetate, lactose, NADH, glucose, formate, glycerin and citrate was analyzed. The results indicated that glycerin had the most significant role, followed by NADH and glucose. On the other hand, lactose inhibited the reduction process [77].

The ways of adaptation and protection of microalgae against the toxic effect of heavy metals involve processes of chelation, exclusion, immobilization and genetic regulation [32]. The integration of metal ions in the cellular metabolism of microalgae involves the formation of complexes between metals and proteins, separation into vacuoles, synthesis of phytochelatins and antioxidant enzymes [32,88]. Phytochelatins are low molecular weight sulfhydryl compounds with which the metal forms complexes with a role in homeostasis and detoxification of the metal. Increasing the concentration of Cd(II) for example, led to a proportional increase in sulfihydryl (-SH) groups [89]. As for the antioxidant compounds used by microalgae, they can be enzymatic (catalase, ascorbate peroxidase, superoxide dismutase, peroxidase and glutathione reductase) and non-enzymatic (cysteine, ascorbic acid, carotenoids, proline and glutathione) [32]. Also, another method of detoxifying the microalgal cell is to pour the metal back into the effluent [34].

Extracellular polymeric substances (SPEs), which are compounds synthesized by microbial organisms, also have an important role in the bioremediation processes. Their structure is formed by proteins and polysaccharides that have functional groups such as hydroxyl, carboxyl and phosphoric amines with a role in forming bonds with metal ions. Analysis of the activity of extracellular polymeric substances (SPEs) synthesized by the freshwater microalga *Chlorella pyrenoidosa* on inorganic arsenic indicated that the interaction between them and the metal ion is achieved by the C-O-H, C-O-C and -NH_2 functional groups of tyrosine and polysaccharide constituents [90]. The algal cell wall is mainly composed of cellulose, but also contains other lipids, polysaccharides, and proteins, and has an overall negative charge on the cell surface. Functional groups with a role in metal ion binding are represented by hydroxyl, carbonyl, carboxyl, phosphate, amino and sulfhydryl groups, groups that determine the negative electrical charge of the cell wall. Bioaccumulation for the removal of heavy metals using microalgae was first suggested in 1957 [91]. Cell wall composition, and implicitly the type of chemical structures available for the metal ions binding is highly influenced by the parameters applied in growing the living organism. Deprivation of microalgae from the necessary light conditions determined the absence of carboxyl groups, and the lack of the necessary amount of nitrogen generated a higher number of carbohydrate and amino groups in the case of tests performed with *Chlorella vulgaris*. Furthermore, a reduced amount of nitrogen generated a higher biosorption capacity when microalgae provided a reduced amount of nitrogen (11.9 mg/g). This is due to the deacetylation amino groups. Metals such as Ca, Fe and Mg are used by the microalgae for its development, while in the case of Cd, the results in the literature differ towards its effect and beneficial or harmful concentrations. Copper in general has shown harmful activity on the electron transport of photosystem I and the modification of PSII [73]. Manganese also has an important role in the metabolism of microalgae having a function in the water cleavage reaction in the photosynthesis process, but zinc has an inhibitory role on chlorophyll synthesis [73].

The cell wall of bacteria has in its structure compounds such as galacturonic acid and teicoic acid which have active functional groups with a role in binding metal ions. Characteristic functional groups and extracellular polysaccharides, which also play a role in the biosorption process, differ depending on the type of bacterium and the culture conditions. Thus, in the case of gram-positive bacteria, phosphoryl and hydroxyl groups be-

come active for heavy metal cations under alkaline conditions, while gram-negative bacteria have phosphate groups in the structure of lipopolysaccharides and phospholipids. Other functional groups involved are amino and carboxyl groups [31,76].

Also, the response mechanism of the bacterial cell to metal ions can be expressed by complexation and precipitation processes. The accumulation of the cadmium, zinc, copper, mercury and calcium using the species *Pseudomonas syringae* was achieved for example by complexation. Precipitation of metals can be achieved through acids such as HPO_4^{2-} produced by *Citrobacter* sp. and H_2S generated by sulfate-reducing bacteria [31]. An important role in the metal ions uptake is therefore ensured by the polysaccharides forming the slippery layer on the outside of the cell wall, as well as other extracellular polymeric substances (SPE) that include lipids, proteins, nucleic acids and carbohydrates. These have the role of stopping the penetration of metals and other harmful external substances or radicals into the intracellular environment [33].

Remediation of heavy metals by bioaccumulation facilitated by bacteria can be achieved mainly by integrating the metal in small amounts into cellular metabolism and by detoxifying excess amounts of metal. Cr(VI) ions can enter the intracellular environment through the sulfate ion channel because the sulfate ion and chromate ion have a similar structure. At the same time, the action of microorganisms on metals consists in reduction or alkylation processes. The reduction of the metal ion Hg(II) to the less toxic form Hg^0 involves the enzymatic transformation facilitated by mercury reductase [31]. Rhamnolipids play an important role in the resistance mechanism of *P. aeruginosa* bacteria, which are synthesized in the late stationary growth phase (96 h).

Cadmium resistance of gram-positive bacteria is facilitated by the ATPase which plays a role in cadmium transport, while for Gram-negative bacteria the Czc system is involved. Studies have also identified a higher incidence of plasmids, especially in bacteria contaminated with heavy metals. The czcABC gene is also involved in activating processes that ensure the resistance of bacteria to heavy metals such as Zn, Cd and Co. This gene has a role in the synthesis of compounds that transport metal ions outside the cellular environment [83].

The structure of the fungal cell wall has a significant influence in the metal removal processes. Its composition includes mannan, glucan and galactan in its outer layer and chitin, cellulose or non-cellulose glucan in its inner layer. The chemical composition of the cell wall also varies depending on the type of fungus. Thus, the cell wall structure of the genus *Aspergillus* lacks chitosan, while *Rhizopus arrhizus* contains more chitin, and *Saccharomyces cerevisiae* has a composition based on the manan-glucan complex and a chitin content of only 1% [92]. Mushroom-specific compounds and structures such as phosphates, polysaccharides, chitin-chitosan complex and glucuronic acid are involved in ion exchange processes that ensure the binding of metals [33]. Starch, amino and hydroxyl groups are the functional groups present in chitin and chitosan compounds with a demonstrated function in removing heavy metals from wastewater [31]. In the case of certain metals, they are reduced by various specific mechanisms. Thus, the proteins ArsC and glutathione reduce arsenate to arsenite [93].

3.2. Factors Affecting Microbial Remediation of Heavy Metals in Wastewaters

In order to obtain maximum metal removal performances in the application of microorganisms as biosorbents, the physico-chemical factors and their effect should be understood and carefully analyzed. Optimization of these parameters leads to the identification of the values that can generate the highest removal performances.

The pH value is an extremely important factor that influences the biosorption and bioaccumulation processes having an effect on the complexation of organic and inorganic ligands, the chemical composition of metal solutions, as well as on redox, hydrolysis and precipitation reactions [68]. Studies have shown generally that the optimal pH values for the proper development of the biosorption process of metal ions through microorganisms ranges from 3 to 6 values [76].

Usually, for the removal of Cr(VI), the maximum efficiency is obtained at pH 2, but this pH value can be destructive for the microbial cell [85]. Various forms of chromium can occur depending on the pH. Thus, $HCrO_4$ form of chromium can be found at pH 1, where it is predominant and at pH 6. Furthermore, $Cr_2O_7^{2-}$ and CrO_4^{2} have been identified starting with pH 6 and above [74,94]. In the case of Pb(II) ions, at a pH lower than 2 the protonation of the functional groups takes place and therefore the efficiency of metal removal decreases.

At the same time, the involvement of the functional groups at the cell wall level in binding of metal ions depends on the pH. Thus, in the pH range 2–5, the carboxyl group is usually activated, and in the range 5–9 both the carboxyl and the phosphate groups are involved. The development of the biosorption process also depends on the properties of the metal: ionic radius, oxidation state and molecular mass [68].

Another important aspect is the influence of other metallic or non-metallic ions on the development of the microorganism remediation process. Understanding it has a major role in treating industrial effluents in which various metallic and ionic species are found. The mechanical strength and declining stability of biomass as it is reused in sorption-desorption cycles are also problems that require finding solutions to enable high-scale application [68]. Eluent selection is of major importance so as to avoid the degradation of functional groups in the biosorbent and to ensure an efficient regeneration [95].

Certain ions can influence the evolution of the process of removing heavy metals by bioaccumulation. Reductase involved in the mechanism of Hg(II) uptake in *Pseudomonas* sp. B50A, for example, is partially inhibited by Ca(II), K(I) and Cu(II) ions. However, other ions such as Sn(II), Cd(II), NH_4(I), Ni(II) and Ba(II) do not influence the enzyme activity [96]. The addition of a 1 mM Cu(II) concentration increased the rate of reduction of Cr(VI) ions to Cr(III) to a maximum of 73%. However, the presence of cadmium, zinc, cobalt and nickel determines a decrease in the reduction process [86]. Also, the remediation process may have a different duration for mono-metallic and multi-metallic solutions. Thus, the equilibrium of the sorption process in the case of bacterial strains isolated from the sediments of a polluted stream, was reached in the first 4 h for the single metal solution, while in the case of the multi-metal solution 5 h were required [97].

The active or inactive form of the bacterium, as well as the development stage of the used organism influences as well the heavy metals sorption process. In the case of *Acinetobacter junii*, the logarithmic phase generated the highest sorption capacity (22.22 mg/g) of Cr(VI) ions, followed by the values obtained for the stationary phase (13.88 mg/g), respectively the non-viable form (6.94 mg/g) [98]. The removal capacity of Cd(II) ions using *Bacillus cereus* was higher in the non-viable form, 31.95 mg/g compared to the viable one, 24.01 mg/g, only 20% of the bioaccumulation process taking place based on intracellular mechanism [99]. In another study that applied the *Bacillus cereus* specie as a biosorbent, the active form generated a better capacity than the inactive form at low concentrations of Cd(II) [100]. The removal of Pb(II) ions using vegetative cells, decaying cells and spores was analyzed by applying the bacterium *Bacillus coagulans*, and the results obtained indicated the highest removal capacity in the case of the vegetative cell [101].

The application of high temperatures (30–45 °C) in the biosorption process causes an increase in metabolic activity of viable microorganisms and thus, implicitly, in the removal efficiency of metals [102]. In the case of applying non-viable microbial forms, the same range of temperature values determines an increase in the available binding sites on the surface of the biosorbent and thus, higher metal uptake. Temperatures above optimum level however, lead to the disintegration of the cell wall functional groups and determines the decrease of metal removal capacity [103]. Identifying the optimal conditions of the experimental parameters is very important to obtain maximum efficiencies in the biosorption process. Values of temperature and stirring speed greater than optimal ones, may cause, for example, the degradation of fungal hyphae [104].

The level of agitation is another factor that must be considered. Optimum value will determine higher metal uptake performance due to the fact that the agitation of the metal solution and the biosorbent facilitates their uniform distribution.

Metal concentration is another important influencing factor in the microbial biosorption or bioaccumulation processes. A higher metal ions concentration leads to a quicker saturation rate of the biosorbent. Also, when living biomass is concerned, the minimum inhibitory concentration must be known, to prevent the loss of viable microorganisms.

Even in the case of metals with metabolic function, quantities that exceed the tolerated limits of microorganisms cause disruption of cellular functions and degradation of components such as cell membrane and DNA structure. Thus, some microorganisms are very resistant to the influence of heavy metals, while others may be sensitive, even at very low concentrations. This depends on the species of microorganism, respectively metal, as well as on external conditions such as pH, temperature, the presence of other ions and electron-yielding functional groups. The tolerance of microorganisms to heavy metals can be found by calculating the tolerance index (TI), respectively the minimum inhibitory concentration (MIC) [71]. The minimum inhibitory concentration represents the lowest pollutant concentration that inhibits the development of the microorganisms [85].

The tolerance index can be obtained based on the following equation [67]:

$$\text{Tolerance Index} = (\text{Hyphae growth of fungi grown in the presence of metals})/(\text{Hyphae growth of control fungi}) \quad (1)$$

Biosorbent dose and cell concentration in biosorption, respectively bioaccumulation processes represent other significant factors influencing metal uptake. Thus, metal removal usually increases with the increasing biosorbent dose or cell concentration up to a specific value, after which overlapping and aggregation of available binding groups can occur [105].

3.3. Heavy Metals Removal Performance

Most of the available studies have applied microorganisms for metal removal from wastewaters in batch mode, especially in single metal systems. Research has shown that the adsorption capacity decreases in multimetal systems in comparison with single metal ones, at least for the same applied contact time. Real effluents contain usually more than one metal ion. Therefore, both single metal and multimetal solutions are important to be analyzed in batch mode.

Microalga *Botryococcus* sp. has been tested for the removal of arsenic, chromium, copper and cadmium from industrial wastewater with efficiencies of 45% for copper, 94% for chromium, respectively values less than 10% for cadmium and arsenic [106]. *Scenedesmus obtusus* microalgae grown in a phosphorus-enriched medium in concentrations of 0, 20, 40, 80, 160 and 320 mg L^{-1}, respectively, was applied as a non-viable form to remove Hg(II) ions on a laboratory scale. The highest adsorption capacity was identified for biomass obtained by culturing in P concentration of 80 mg L^{-1}, but the highest growth rate of microalgae biomass was obtained at a P concentration of 160 mg L^{-1} [107]. Also, a difference in the removal capacity of metals was noticed between autoflocculating and non-flocculating microalgae. Thus, the removal of Cd(II) ions was performed with a higher efficiency (93.39%) by *Scenedesmus obliquus* with autoflocculation capacity, in the range of pH values 3–6 and a biomass dose of 0.8 g/L [108].

Several types of sorbents obtained based on the microalga *Scenedesmus quadricauda* were used to determine the adsorption capacity, respectively absorption of Cr(VI) ions. The microalgal biosorbent in powder form had a Cr(VI) removal efficiency of 96.62%, approximately double then that of the microalgal pellets used. At the same time, the application of chemical treatments to the inactive biomass did not facilitate the increase of the efficiency of the biosorption process, and in the case of using microalgae in active form, a significantly lower uptake performance was generated than in the case of the inactive organism, 67.03%, value obtained after 12 days of bioaccumulation. Biocarbon obtained by pyrolysis at 500 °C demonstrated the total removal of the target metal [28].

The adsorption capacity of bacterial-based biosorbents was also tested by applying natural effluent and real wastewater tests. Removal of some heavy metals ions from wastewater using a concentration of 0.2 g/L biosorbent, temperature 25 °C, actual effluent pH value and 0.5 M HNO_3 as eluent, was analyzed from a water collected from the confluence between the effluent of a wastewater treatment plant and domestic wastewater from China. The results indicated removal efficiencies of 70.6%, 89.6% and 94.8%, for Cu(II), Cd(II), respectively Pb(II), but for Ni(II) and Cr(IV) the identified values were less than 10% [109]. Table 1 synthesizes several significant results identified in recent scientific literature on heavy metals removal performance using microbial living biomass.

Table 1. Heavy metals removal by microbial living biomass.

Microorganism	Metal	Optimal Conditions	Efficiency/ Sorption Capacity	Ref.
MICROALGAE				
Chlorella vulgaris	Hg(II)	C_i = 10 µg/L, pH = 5.0 ± 0.2, t = 5 days	62.85% -	[110]
Phacus sp.	Pb(II)	C_i = 1 mg/L, 10% (*v*/*v*) *Phacus* strain inoculum, culture concentration = 1.03 × 10^6 cells/mL, room temperature (25 °C), t = 1 week	96.8% 3.90 ± 0.09 mg/g	[111]
Phacus sp.	Al(II)	C_i = 9.94 mg/L, 10% (*v*/*v*) *Phacus* strain inoculum, culture concentration = 1.03 × 10^6 cells/mL, T = 25 °C, t = 1 week	19% 12.32 ± 0.13 mg/g	[111]
Phacus sp.	Ni(II)	C_i = 9.94 mg/L, 10% (*v*/*v*) *Phacus* strain inoculum, culture concentration = 1.03 × 10^6 cells/mL, room temperature (25 °C), t = 1 week	75.17% 30.8 ± 0.16 mg/g	[111]
BACTERIA				
Pseudomonas sp. B50A	Hg(II)	C_i = 350 mM; Cell concentration = 2 × 10^7 CFU mL^{-1}, T = 30 °C; pH = 8; t = 8 h	93% -	[96]
Stenotrophomonas sp.	Pb(II)	C_i = 200 mg/L; pH = 7; T = 37 °C; Agitation speed (rpm) = 150	85.3% -	[102]
Bacillus coagulans		C_i = 50 mg/L; pH = 5; T = 23 °C; D = 1 g/L; t = 6 min; Agitation speed (rpm): 160	- 17.53 mg/g	[101]
Bacillus xiamenensis		C_i = 100–200 mg/L; pH = 6; T = 35 °C; D = 1 g/L; t = 144 h; Agitation speed (rpm) = 140	99.19% 216.75 mg/g	[112]
Acinetobacter junii	Cr(VI)	C_i = 100 mg/L; pH = 2; T = 27 °C; D (g/L) = 2; t = 120 min	44.4% (logarithmic phase), 27.7% (stationary phase) 22.22 mg/g (logarithmic phase), 13.88 mg/g (stationary phase)	[98]
Stenotrophomonas sp.		C_i = 100 mg/L; pH = 8; T = 37 °C; Agitation speed (rpm) = 150	68.54% -	[102]
Klebsiella pneumoniae			65.98% -	
Staphylococcus sp.			71.45% -	
Stenotrophomonas sp.	Ni(II)	C_i = 200 mg/L; pH = 7; T = 37 °C; Agitation speed (rpm) = 150	48.78% -	[102]
FUNGI				
Saccharomyces cerevisiae	Hg(II)	C_i = 79.8 µg/L; pH = 5.45 D = 47.7 × 10^7 CFU;	99.4% -	[113]

Aspergillus flavus	Hg(II)	C_i = 10 mg/L; T = 30 °C; pH = 4.13 (shaken system), respectively 4.01 (static system); D = 108 spore/mL fungal spore suspension; dry mass = 14.9 g/L (shaken system), respectively 14.3 g/L (static system)	97.50% (shaken system); 98.73% (static system) 6.55 Hg (mg/L)/g dry weight (shaken system); 6.91 Hg (mg/L)/g dry weight (static system)	[66]
Aspergillus fumigatus and *Aspergillus flavus* (consortium)	Cd(II)	C_i = 100 mg/L; pH = 5; T = 30 °C; D = 6%; t = 144 h Agitation speed (rpm) = 120;	82.21 ± 1.00% 5.51 ± 1.23 mg/g	[114]
Trichoderma sp.	Cu(II)	Temperature (°C): 27 ± 3 °C; pH: 6.5; Agitation speed: 200 rev.min^{-1}; Contact time (h): 144	80% 19.6 mg/g	[115]
Aspergillus niger	Cr(III)	C_i = 240 mg/L; pH = 5.3, respectively 5.5; T = 30 °C; D = 0.3 g/100 mL; Optimum nutrients dose = 1 g/L urea; Agitation speed = 150 rpm	72% 185 mg/g	[116]
Aspergillus oryzae			67% 208 mg/g	
Cladosporeum perangustumm, *Penicillium commune*, *Paecilomyces lilacinus*, *Fusarium equiseti* (consortium)	Cr(VI)	pH = 4; T = 28 °C; t = 48 h	73.73% -	[117]
Aspergillus flavus and *Aspergillus fumigatus* (consortium)		C_i = 100 mg/L; pH = 5; T = 30 °C; Optimum inoculum size = 6%; Agitation speed = 120 rpm; t = 144 h	81.25 ± 0.25% 5.78 ± 1.17 mg/g	[114]

C_i = Initial concentration, t = Contact time, T = Temperature, D = Biosorbent dose.

As far as fungi sorbents are concerned, simultaneous removal of Cr, As and Cd metals by applying the fungal species *P. chrysosporium* produced a removal efficiency of 9.28 mg/L, 14.15 mg/L, respectively 4.53 mg/L at optimal values of 30 °C, 120 rpm and the equilibrium time of one hour. At the same time, the results obtained for the individual biosorption of each metal indicated for arsenic a double efficiency, whereas in case of cadmium a four times higher performance was observed [104]. Five fungal strains in viable form (*Aspergillus terreus* AML02, *Paecilomyces fumosoroseus* 4099, *Beauveria bassiana* 4580, *Aspergillus terreus* PD-17 and *Aspergillus fumigatus* PD-18, respectively) were used to study the remediation process of multi-metal solution containing Cd, Cr, Cu, Ni, Pb and Zn. For an initial concentration of 30 mg/L, the highest accumulation capacity of the metal solution was determined for *B. bassiana* (26.94 ± 0.07 mg/L) and *A. fumigatus* (27.59 ± 0.09 mg/L). Moreover, the use of *Aspergillus fumigatus* has reduced the concentrations of metals Cd, Cu, Ni, Pb and Zn to values that meet the limits imposed by the FAO (Food and Agriculture Organization) for irrigation water. Also, it was noticed in the case of exposure to the multimetallic solution the increase of the duration of the lag phase of development of the fungal species used, from 6–7 h to 17–18 h [118]. A comparative study of chromium removal using *Penicillium chrysogenum* and *Aspergillus niger* species indicated a higher efficiency of the remediation process for viable forms [81]. Furthermore, the removal of Cd(II) concentrations of 162.71 ± 1.3 mg/L and 81.39 ± 2.58 mg/L from real effluents was achieved in a proportion of 69.1 ± 0.19% and 72.05 ± 1.40%, respectively, by applying a consortium of fungi comprising *Aspergillus flavus* and *Aspergillus fumigatus* in active form [114].

As in the case of other microorganisms, also for fungal species such as *Aspergillus niger* applied for the removal of Cu(II) and Pb(II) ions, two phases of the biosorption process were observed, namely a shorter phase (10–20 min), followed by a phase of gradual increase or decrease of the biosorption efficiency correlated with the transport of the metal through the cell membrane or intracellular diffusion with reduced speed through the cell wall [119]. Table 2 synthesizes some results identified in recent research studies regarding the removal of heavy metals by microbial inactive biomass.

Table 2. Heavy metals removal by microbial inactive biomass.

Microorganism	Metal	Optimal Conditions	Efficiency/ Sorption Capacity	Ref.
		MICROALGAE		
Scenedesmus obtusus	Hg(II)	C_i = 20–200 mg/L; pH = 5; T = 25 °C; D = 0.125 g/L; t = 3 h	- 95 mg/g	[107]
Scenedesmus quadricauda	Pb(II)	C_i = 10 mg/L; pH = 5; room temperature; D = 0.2 g/L; t = 1 h	82% -	[95]
Scenedesmus quadricauda	Cd(II)	C_i = 10 mg/L; pH = 5; room temperature; D = 0.2 g/L; t = 1 h	66% -	[95]
Scenedesmus obliquus		C_i = 50 mg/L; pH = 6; T = 30 °C; D = 1 g/L	- 68.6 mg/g	[120]
Spirulina platensis (raw biomass)	Cr(VI)	C_i = 50 mg/L; pH = 1; T = 60 °C; D = 0.2 g/L; t = 1.5 h	93% -	[121]
Spirulina platensis (biodiesel production waste)			70% 45.5 mg/g	
Scenedesmus quadricauda (powder)		C_i = 1 mg/L; pH = 2; T = 22 °C; D = 2 g/L; t = 3 h	96.62% -	[28]
Scenedesmus quadricauda (biochar)		C_i = 1 mg/L; pH = 2; T = 22 °C; D = 2 g/L; t = 3 h	100% 25.19 mg/g	[28]
Scenedesmus sp.		C_i = 10 mg/L; pH = 1; T = 30 °C; D = 10% (*w*/*v*); t = 2 h; Particle size = 60 μm; Agitation speed = 300 rpm	92.89% -	[122]
		BACTERIA		
Bacillus licheniformis	Hg(II)	C_i = 50 mg/L; pH = 7; T = 30 °C; D = 0.5 g/L; t = 1 h	70% -	[123]
Bacillus licheniformis	Pb(II)	C_i = 200 mg/L; pH = 6; T = 20–22 °C; D = 0.7 g/L; t = 12 h	98% 113.84 mg/g	[124]
Pseudomonas putida I3		C_i = 100 mg/L; pH = 5; T = 25 °C; D = 0.2 g/L; t = 1 h	- 345.02 mg/g	[109]
Bacillus xiamenensis		C_i = 100–200 mg/L; pH = 6; T = 35 °C; D = 1 g/L; t = 6 h; Agitation speed (rpm) = 140	97.18% 207.4 mg/g	[112]
Bacillus cereus	Cd(II)	C_i = 200 mg/L; pH = 6; T = 35 °C; t = 20 h	82% -	[125]
Bacillus megaterium		C_i = 100 mg/L; pH = 4; T = 30 °C; D = 3 g/L; t = 2 h	90% 15.1 mg/g	[126]
Brevundimonas sp. ZF12		C_i = 50 ppm; pH = 6; T = 30 °C; t = 1 h	60% 49.01 mg/g	[76]
Sulphate reducing bacteria	Cd(II)	pH = 8; T = 35 °C; t = 24 h 0.015 g SRB (dry weight)/g beads (dry weight)	- 160 mg/g	[127]
Bacillus laterosporus	Ni(II)	C_i = 10–20 mg/L; pH = 7; T = 30 °C; D = 40 g/L; t = 2 h	- 44.44 mg/g	[128]

Acinetobacter junii	Cr(VI)	C_i = 100 mg/L; pH = 2; T = 27 °C; D = 2 g/L; t = 120 min	- 6.94 mg/g	[98]
		FUNGI		
Aspergillus niger	Pb(II)	C_i = 200–1400 ppm; pH = 4–5.4; T = 37 °C	- 3.25 to 172.25 mg/g	[119]
		C_i = 10, 50,100 mg/L; pH = 5; T = 30 °C; D = 70 g/L; t = 1.5 h	- 137.3 mg/g; 398.3 mg/g; 564 mg/g	[129]
Fusarium sp. (two strains)		C_i = 90 mg/L; pH = 6; T = 49,85 °C; D = 1 g/L; t = 1 h; Agitation speed (rpm) = 150	- 232.56 (ZSY strain), 263.16 mg/g (MJY strain)	[130]
Saccharomyces cerevisiae	Cd(II)	C_i = 50 mg/L; pH = 6; T = 40 °C; D = 5 g/L; Agitation speed (rpm): 150	- 7.252 mg/g	[131]
Trichoderma sp.	Cu(II)	T = 27 ± 3 °C; D = 3 g/L; t = 4 h Agitation speed = 200 rev.min^{-1}	- 23.01 mg/g	[115]
Penicillium griseofulvum	Cr(VI)	C_i = 67.8 mg/L; pH = 2; T = 27 °C; D = 2 g/L; t = 37.5 min	79.9% 75.1 mg/g	[132]

C_i = Initial concentration, t = Contact time, T = Temperature, D = Biosorbent dose.

4. Bioremediation of Persistent Organic Pollutants Contaminated Wastewaters by Microorganisms

4.1. Mechanisms of Persistent Organic Pollutants Removal by Microorganisms

The POPs released in environment either are accumulated and biomagnified along the food chain or are transformed under the action of biotic and abiotic factors into modified, less complex and less toxic organic compounds [2,133–135].

Understanding the metabolic pathways involved in microbial degradation of persistent organic pollutants will expand our ability to enhance the remediation process of wastewaters. Due to the POPs structural complexity, the free cells of tolerating microorganisms are able to remove the pollutants from aqueous solutions by one or more mechanisms [35,134,136–138] (Figure 7) described as:

- biosorption (I),
- bioaccumulation (II),
- cometabolism (III),
- biotransformation (IV),
- biomineralization (V) and
- extracellular biodegradation (VI).

Biosorption is the mechanism independent of metabolic activities of microbial cell [53] which is based on the interaction of persistent organic pollutant molecules with functional groups found in the cell wall constituents (e.g., carboxyl, phosphoryl, amine etc.) [24,35,139] and/or on the retention of persistent organic pollutants molecules on the biosorbent surface due to hydrophobic interaction and van der Waals forces [139]. In the biosorption process, the microbial biomass used is frequently inactivated by thermal processes, but some researchers also use freeze-dried biomass [139]. The interactions realized between microbial biomass and POPs depend on the chemical structure and proprieties of a particular POPs, as well as the specific chemistry of the microbial biomass [24,139]. According to Aksu [139] "*the size of cells, morphology and chemical composition as well as the number of the active adsorption sites and POPs distribution and molecular size and reactivity as well as their mobility in the solution phase*" can significantly affect the pollutant retention performance. For the majority of microbial biosorbents, the cell surface is negatively charged due to the higher proportion of carboxyl, phosphoryl, amine and other functional

groups in the cell wall compounds and pollutants with cationic groups are actively attracted through electrostatic interaction [24]. *Escherichia coli*, *Zooglea ramigera*, *Bacillus megaterium*, *Bacillus subtilis*, *Zoogloea ramigera*, *Rhizopus oryzae*, *Mucor racemosus*, *Rhizopus arrhizus*, *Sporothrix cyanescens*, *Emericella nidulans*, *Bacillus pumilus* are some of microbial strains studied for lindane, pentachloronitrobenzene, 2,4-dichlorophenoyacetic acid, 1,2,3,4-tetrachlorodibenzo-*p*-dioxin, or polychlorinated dibenzofurans biosorption [139–144].

The study conducted by Bell and Tsezos [141] asserts that lindane, pentachlorophenol and 2-chlorobiphenyl are removed by *Rhizopus arrhizus* inactivated biomass by physical mechanisms (adsorption). According to the Ju et al. [140] study, hydrophobic interaction and van der Waals forces are involved in the biosorption of lindane by *Escherichia coli*, *Zooglea ramigera*, *Bacillus megaterium*, *Bacillus subtilis*. In another study, the lindane is removed by heat treated *Rhizopus oryzae* by "*physical bonding of the negatively charged lindane molecule to the negatively charged fungal cell wall with hydrogen ions acting as the bridging ligand*" [142]. The dead and live biomass of *Bacillus pumilus* was used for removal of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin and some polychlorinated dibenzofurans. The study conducted by Hong et al. [143] proved that dead biomass of *Bacillus pumilus* remove more effectively the POPs studied than live cells.

Bioaccumulation is the mechanism by which POPs after their penetration inside the cells of microbial species, bioconcentrate without changing their structure [145]. In general, the POPs that penetrate inside cells undergo some transformations that result in insoluble metabolites that are subsequently bioaccumulated [146–152]. The analysis of the published studies shows that the most part of the studied microorganisms have the ability to metabolize POPs and not to bioaccumulate them inside their cells. *Azospirillum lipoferum* is one of the microbial strains able to remove dicofol by bioaccumulation and thus enhance the persistence of this pollutant in soil [153].

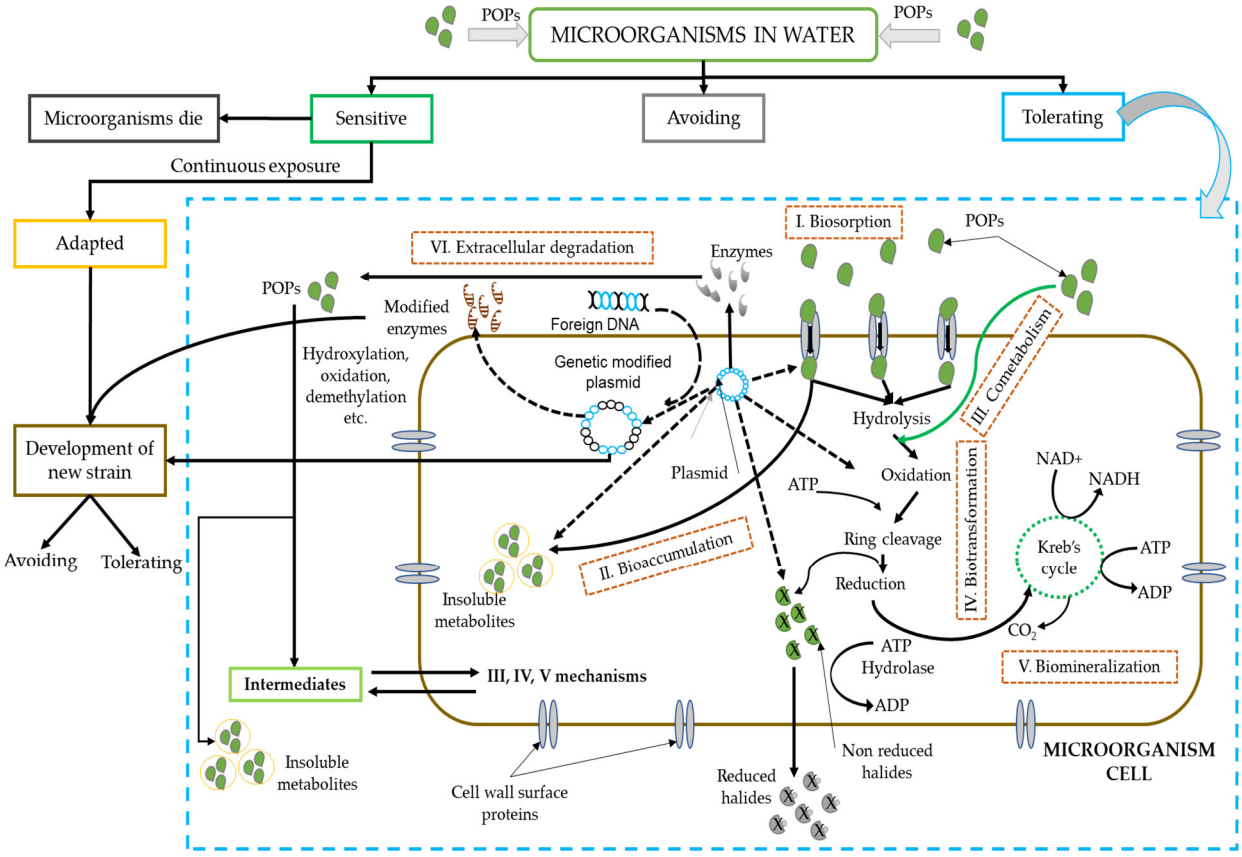

Figure 7. POPs removal strategy followed by microorganisms: the bioremediation mechanisms followed during the interaction between microorganism cell and POPs.

Biodegradation of POPs based enzymes is one of the most important mechanism involved in microbial bioremediation of liquid environment contaminated with POPs. Various classes of transferase, isomerase, hydrolase and other enzymes catalyze the hydrolysis, oxidation/reduction, addition of oxygen to a double bond, oxidation of amino group ($-NH_2$) to a nitro group, hydroxyl group addition to a benzene ring, dehalogenation, reduction of a nitro group (NO_2), sulphur replacement with oxygen, metabolism of side chains, ring cleavage, etc. The biodegradation of POPs mediated by enzymes can take place either inside or outside the microbial cells. The intra- or extracellular biodegradation by enzymes depends significantly on the solubility of xenobiotics compounds. Gianfreda et al. [154] ascertain that the soluble POPs can easily enter in cells and thus interact with intracellular enzymatic systems, but the insoluble substances cannot enter cells being firstly extracellular transformed into soluble or easily cell available products.

Extracellular biodegradation of POPs occurs as a result of the interaction between pollutant and extracellular enzymes and glycoconjugates released by cells [155,156]. Oxidoreductases, oxygenases, monooxygenases, dioxygenases, laccases, peroxidases are the main extracellular enzymes released by microorganisms, involved in the detoxification of toxic organic compounds [157,158]. Since there are POPs with very low solubility in water and high molecular mass for their extracellular biodegradation, the microorganisms release hydrolytic enzymes which disrupt major chemical bonds [157]. Examples of such enzymes are: lipases, cellulases, proteases, hemicellulose etc. [157,158]. The extracellular glycoconjugates involved in POPs removal are rhamnolipids, sophorolipids, exopolysaccharides, glycoproteins and glycol-lipopeptides [156] which are deliberately released by the cells as a result of normal metabolic activity or as a result of the cell defense system activation against pollutant toxicity [156,159]. The glycoconjugates produced by microbial strains facilitate the uptake of the POPs, enhance the biodegradation of hydrophobic pollutants, reduce the surface and interfacial tension etc. [156].

The results of the majority of studies focused on the identification of intracellular enzymes showed the involvement of cytochrome P450 family (CYP) epoxidases and transferases enzymes in intracellular biodegradation of persistent organic pollutants [160]. The cytochrome P450 enzymes have been shown to be the catalysts of hydroxylation, heteroatom oxygenation, dealkylation, epoxidation of C = C bonds, reduction and dehalogenation reactions [160]. Cytochrome P450 have been identified as responsible for biodegradation of hexabromocyclododecane and 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane by *Rhodopseudomonas palustris* [147], respectively *Trichoderma hamatum* FBL 587 [161]. The main types of enzymes involved in the biodegradation of POPs as well as the genes which encoding the enzymes are presented in Table 3.

Dalton and Stirling [162] defined the cometabolism of organic substances as "*the transformation of non-growth-substrate in the obligate presence of a growth-substrate or another transformable compound*". The cometabolism reactions involved in organic pollutant biodegradation are catalyzed by oxygenase enzymes secreted by microorganisms [163]. Examples of such enzymes are: methane-mono-oxygenase (MMO), mono- and dioxygenase, ammonia mono-oxygenase and biphenyl oxygenase [163]. According to Alvarez et al. [164] "*even the most persistent organic pollutant can be metabolized to some extent by microbial cultures, either by utilization of the compounds as a source of energy or nutrients, or by cometabolism with other substrates supporting microbial growth*". Microorganisms such as of *Bacillus cereus* HWB1, *Pseudomonas taiwanensis* ECAe22, *Fusarium verticillioides* AT-100, *Pseudoxanthomonas* sp., *Janibacter* sp. have biodegraded 4-chlorophenol, 4-nitrophenol, lindane, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and pentaclorophenol with high efficiencies only in the presence of carbon sources such as yeast extract, *A. tequilana* leaves, glucose, succinate, starch, dextrin and maltose [148–150,165–167]. These results actually show that the biodegradation of persistent organic pollutants by microbial strains was mainly achieved through a cometabolic mechanism.

A variety of microbial strains have the capacity to degrade the POPs by reduction, oxidation, hydrolysis, dehalogenation, and methylation reactions catalyzed by enzymes.

These reactions lead to a complete or partial mineralization of POPs and which result in a wide variety of metabolites, CO_2 and energy. The metabolic pathways involved in biotransformation of POPs depend on the type of pollutant as well as microbial strain. *Rhodotorula* sp. VITJzN0 was able to transform the lindane in γ-pentachlorocyclohexane, 1,3,4,6-tetrachloro-1,4-cyclohexadiene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, chloro-*cis*-1,2-dihydroxycyclohexadiene, 3-chlorocatechol, maleylacetate following dechlorination, dehydrochlorination, oxidation reactions [168]. *Stenotrophomonas maltophilia* OG2 by hydrolysis transformed endosulfan in endosulfan diol, endosulfan ether and endosulfan lactone [151].

Table 3. The POPs metabolizing enzymes of microbial strains.

POPs	Genes Encoding Enzymes	POPs-Metabolizing Enzymes
Polychlorinated dibenzo-p-dioxins	*dxnA1*, *dxnA2*, *fdx1* and *redA2* [169]	Dioxygenase, cytochrome P450, lignin peroxidase, dehalogenase [170], 2-haloacid dehalogenase [171], carbazole 1,9a-dioxygenase, aromatic ring hydroxylating dioxygenase [169]
Lindane	*Lin* genes [172,173]	Permease, ATPase, periplasmic protein and lipoprotein [172], dehydrochlorinase, halidohydrolase, dehydrogenase, dechlorinase, ring-cleavage dioxygenase, maleylacetate reductase, phosphoesterases and catechol 1,2-dioxygenase [173], lindane dechlorinase, lindane dehalogenase, DCHQ reductive dechlorinase, Mn peroxidase and lignin peroxidase [174]
Endosulfan	*Ese* gene [175]	Esd monooxygenase [175]
Pentachlorophenol	*pcpA*, *pcpB*, *pcpC*, *pcpD* and *pcpE* [176,177]	PCP hydroxylase (PcpB) and PcpD (TCBQ reductase), TCHQ dehalogenase, 2,6-dichlorohydroquinone dioxygenase, maleylacetate reductase [176,177]
Hexabromocyclododecane	*LysR, GST, Cyt C, p450, HADH, RegA, CcoN, CcoO, CcoP* and *CcoQ* [147]	Haloalkane dehalogenases linA2 and linB [178], fluoroacetate dehalogenase, protocatechuate 4,5-dioxygenase, dioxygenase, peroxidase, P450 monooxygenase and dehalogenase [147]
Decabromodiphenyl ether (BDE 209)	*Alcohol dehydrogenase genes, COG0625 (Glutathione S-transferase gene), COG2124 (Cytochrome P450 enzymes gene), COG0778 (nitroreductase gene) COG3805 (aromatic ring-cleaving dioxygenase gene)* and *COG0596 (predicted hydrolases* or *acyltransferases (alpha/beta hydrolase superfamily gene))* [179]	Biphenyl 2,3-dioxygenase, catechol 2,3-dioxygenase, cytochrome P450/NADPH-cytochrome P450 reductase, glutathione S-transferase and nitroreductase/dihydropteridine reductase [179]
1,1,1-Trichloro-2,2-bis(4-chlorophenyl) ethane (DDT)	*ProtID g128, ProtID g8100, ProtID g3303, ProtID g1796* and *g8655, ProtID g8027, ProtID g5890, ProtID g1645*, *ProtID g3541* [161]	Dioxygenase and lignin peroxidase [180], epoxide hydrolases, FAD-dependent monooxygenases, glycosyl- and glutathione-transferases, cytochrome P450 monooxygenase sdnT, cytochrome P450 monooxygenase, superoxide dismutase, DyP-type peroxidase, putative secreted hydrolase [161]

4.2. Factors Affecting Microbial Remediation of POPs in Wastewaters

The normal metabolic activity of microbial strains during the bioremediation of POPs could be affected by a diversity of factors, which can be grouped as [136,181]:

- Abiotic factors (environmental conditions such as: ambient temperature, pH of liquid medium, available nutrients, contact time between pollutant and microbial strain, inoculum size [145,168,182,183], the presence of oxygen etc. [183].
- Biotic factors (e.g., plasmid-encoded genes, bacterial chemotaxis, complex multispecies interactive networks etc.)[136],
- Factors related to the pollutant proprieties: chemical nature, toxicity, initial concentration of POPs in liquid medium, availability, solubility etc. [181].

According to the data of many researchers, biodegradation of POPs can occur in a wide pH range, but for the main microorganisms it was observed that the optimum pH value is 7 [148,166,174,184–190]. Since the biodegradation of POPs is dependent on the cellular metabolism, the best performances for POPs biodegradation were obtained mostly at the optimum pH for microbial strain growth. For example, at pH value of 7 the microorganisms *Kocuria* sp. DAB-1Y, *Staphylococcus* sp. DAB-1W, *Sphingobium japonicum* have the highest performance both for growth and for biodegradation of lindane (efficiencies up to 94%) [185]. Also, *Bacillus cereus* HWB1 and *Pseudomonas taiwanensis* ECAe22 have the same optimal pH value for both cell growth and 4-Chlorophenol and 4-Nitrophenol biodegradation [166]. Decabromodiphenyl ether (BDE 209) was biotransformed with efficiencies of 55.16% and 56% by *Stenotrophomonas* sp. strain WZN-1[149], respectively by *Pseudomonas aeruginosa* [150] at initial pH of 5, respectively 7.5. Lu et al. [191] highlighted that at pH above 6, the dicofol compound was biodegraded by *Microbacterium* sp. D-2 with a rate above than 70%, the maximum of 81.9% being reached at pH 7. So, based on published researches, the biodegradation of POPs by microorganisms is most favorable under a neutral range of pH (between 6 and 8) [165,167,192–194].

In case of temperature, the optimal value at which the best results of POPs biodegradation by microbial strains are obtained is in the range of 25–37 °C [149,184,190,195–197], but most often, the suitable value of temperature is 30 °C [146,148,150,165–168,174,185–189,191,193,198–201]. Due to the fact that microbial metabolism significantly depends on temperature, Bajaj and Singh [37] ascertain that at temperatures below 20 °C, most microorganisms extremely reduce their activity in mesophilic enzymes, causing thus high activation energy, low kinetic energy and slower conformational movements. Also, under cold conditions the viscosity of POPs increases, their volatilization decreases and their bioavailability is reduced [37]. However, there are species of microorganisms that are able to biodegrade persistent organic pollutants even at temperatures below 20 °C. Such examples are *Rhodococcus erythropolis* P25 which degraded 26% of phenanthrene at 15 °C, in 20 days and 17.1% and 16.0% at 5 °C, respectively 25 °C [202]. Another psychrophilic strain is *R. erythropolis* S-7 which completely degraded 3-chlorobenzoate at 10, 20 and 30 °C. However, the faster biodegradation rate occurred at 20 °C [194]. *Sphingobium indicum* B90A degraded 48.8% of 25 mg/L of lindane at 4 °C and 97.2% at 30 °C [203]. *Pseudoalteromonas*, *Psychrobacter* and *Arthrobacter* genera isolated from Antarctic seawater sample were able to remove polychlorinated biphenyls with efficiencies between 35.6% and 79.8% at 4 °C and between 0.4% and 82.8% at 15 °C [204].

The concentration level of the target pollutant in liquid medium can significantly affect the biomass production as well as the POPs degradation rates [168,174,192]. In their paper, Kumar and Pannu [192] ascertain that a low pollutant concentration in liquid medium sometimes is not enough to activate the secretion of enzymes directly involved in the degradative reactions, while high levels may be toxic to the microorganisms [205]. The strain *Candida* VITJzN04 has the ability to tolerate lindane, finding that up to 600 mg lindane/L this species degraded completely the pollutant, turning it into a source of

energy and thus facilitating biomass production. At 100 mg lindane/L, the biomass production was about 1.3 g/L and at 600 mg lindane/L was more than 2.9 g/L [174]. The level of pollutant at which microorganisms tolerate a specific POP depends both on the type of pollutant and the microorganism specie. For example, *Kocuria* sp. DAB-IY and *Staphylococcus* sp. DAB-1W are able to tolerate lindane up to an initial concentration of 100 mg/L [185], *Rhodotorula* sp.VITJzN03 up to 600 mg/L [168] and *Microbacterium* sp. P27 no more than 50 mg lindane/L [187]. Pentachlorophenol was biodegraded with efficiencies above 99% by *Janibacter* sp. [167] and *Pseudomonas fluorescens* [199] for initial concentration up to 500 mg/L, respectively 200 mg/L and *Cunninghamella* sp. UMAS SD12 at 20 mg PCP/L had a maximum degradation efficiency of only 51.7% [197]. Variation of 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane (DDT) concentration between 10 and 50 mg/L does not inhibit the biomass production of *Serratia marcescens* NCIM 2919, but its biodegradation capacity is up to 42% [206].

The kinetic studies have shown that the biodegradation rate of POPs is closely correlated with microorganism strain [184,186–188,191], the pollutant proprieties, but also with their concentration in the liquid media [191,205,207]. At concentrations up to 50 mg pentachlorophenol/L, *Janibacter* sp. was able to remove almost the entire quantity of PCP after 72 h of incubation time, but at concentrations higher than 200 mg/L a longer contact time is required for a complete removal of the pollutant [167]. After 8 days of contact time the strains *Kocuria* sp. DAB-1Y, *Staphylococcus* sp. DAB-1W and *Sphingobium japonicum* removed 94–98% of lindane amount corresponding to the initial concentration of 10 mg/L [185]. *Paracoccus* sp. NITDBR1 after the same contact time was able to remove 90.6% of 100 mg lindane/L [188]. For a complete removal of 600 mg lindane/L, the strain *Candida* sp. VITJzN04 [174] required a minimum contact time of 6 days, while *Rhodotorula* sp. VITJzN03, 10 days [168].

Another factor that may have significantly positive or negative effects on biodegradation is the availability of nutrients in liquid medium. Dey et al. [166] showed in their study that the biodegradation capacities for 4-chlorophenol and 4-nitrophenol of *Bacillus cereus* HWB1 and *Pseudomonas taiwanensis* ECAe22 were enhanced by increasing the yeast extract concentration in liquid medium from 0.1 to 0.3%. In another study, the biodegradation of lindane by *Fusarium verticillioides* AT-100 strain was improved by addition of 12 g/L *A. tequilana* leaves in a medium consisting of $(NH_4)_2SO_4$, Na_2HPO_4, KH_2PO_4, Tween 20, $CusO_4{\cdot}5H_2O$ and elemental iron [148]. The importance that glucose exerts on the biodegradation performance of POPs by microorganisms was highlighted by the studies conducted by Wang et al. [165] and Khessairi et al. [167]. The addition of 100 mg in 1 L of minimal salt medium improved the *Pseudoxanthomonas* sp. biodegradation capability for 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) from 10.2% to 95% [165]. *Janibacter* sp. in minimal salt medium supplemented with 1% glucose degraded more than 90% of 20 mg pentaclorophenol/L in 72 h [167]. Wang et al. [165] specified that the succinate, starch, dextrin and maltose, could also promote the biodegradation of DDT. The results of these studies indicate that the cometabolism is the main mechanism involved in microbial degradation of the mentioned POPs.

4.3. Persistent Organic Pollutants Removal Performance

Both viable and inactivated biomass of some species of bacteria and fungi were studied for the removal of POPs from liquid media considering the influence of various factors such as pH, initial pollutant concentration, contact time, agitation speed for flask mixing and temperature. Studies focusing on the removal of POPs by inactivated biomass from microorganisms are few and have been conducted until 2005. In recent years, the majority of researchers have been focused on studying the ability of viable biomass to remove POPs and microbial strains such as *Bacillus* sp., *Pseudomonas* sp., *Stenotrophomonas* sp., *Candida* sp., *Rhodotorula* sp. etc. which have shown to have the potential to biodegrade some types of POPs. Thus, in Table 4 are presented the results of some studies whose

purpose was to study the biodegradation of POPs by viable biomass, while in Table 5 the performances of inactive microbial biomass in POPs removal are shown.

Table 4. Persistent organic pollutant removal by living microorganisms.

Microorganism	POPs	Optimal Conditions	Efficiency/ Sorption Capacity	Ref.
BACTERIA				
Bacillus subtilis MF447840.1	4-chlorophenol	pH = 7.4, Ci = 1000 mg/L, t = 40 h, T = 37 °C, agitation speed = 150 rpm	100% -	[196]
Azospirillium barasilense	Dicofol	pH = 7, Ci = 100 mg/L, t = 28 days, T = 27 ± 1 °C	75% -	[184]
Azotobacter chroococcum			94% -	
Klebsilense pneumoneae			88% -	
Pseudomonas cepacia			87% -	
Bacillus subtilis			85% -	
Pseudomonas fluorescens			82% -	
Bacillus polymyxa			84% -	
Microbacterium sp. D-2	Dicofol	pH = 7, Ci = 50 mg/L, t = 24 h, T = 30 °C, agitation speed = 180 rpm	85.1% -	[191]
Kocuria sp. DAB-1Y	Lindane	pH = 7, Ci = 10 mg/L, t = 8 days, T = 30 °C, agitation speed = 120 rpm	94%	[185]
Staphylococcus sp. DAB-1W			98%	
Sphingobium japonicum			98%	
Achromobacter sp. A3	Lindane	pH = 7, Ci = 50 mg/L, t = 15 days, T = 30 °C, agitation speed = 150 rpm	88.7 ± 1.24% -	[186]
Microbacterium sp. P27	Lindane	pH = 7, Ci = 50 mg/L, t = 15 days, T = 30 °C, agitation speed = 150 rpm	82.7 ± 1.79% -	[187]
Paracoccus sp. NITDBR1	Lindane	pH = 7, Ci = 100 mg/L, t = 8 days, T = 30 °C, agitation speed = 120 rpm	90.6% -	[188]
Bacillus subtilis	Endosulfan	pH = 6.5, Ci = 50 mg/L, t = 7 days, T = 30 °C, agitation speed = 130 rpm	94.2% -	[208]
Bacillus subtilis	Endosulfan	pH = 7, Ci = 10 mg/L, t = 35 days, T = 30 °C, agitation speed = 130 rpm	94.5% -	[189]
Stenotrophomonas sp. strain WZN-1	decabromodiphenyl ether (BDE 209)	pH = 5, Ci = 65 μg/L, t = 30 days, T = 25 °C,	55.15% -	[149]
Pseudomonas aeruginosa	decabromodiphenyl ether (BDE 209)	pH = 7.5, Ci = 1 mg/L, t = 7 days, T = 30 °C, agitation speed = 150 rpm	56% -	[150]

Pseudomonas sp. strain HB01	γ-hexabromocyclododecane	pH = 7, Ci = 1 mM, t = 5 days, T = 28 °C, agitation speed = 150 rpm	81% -	[190]
Pseudoxanthomonas sp.	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT)	pH = 7.5, Ci = 20 mg/L, t = 72 h, T = 30 °C, agitation speed = 150 rpm	95% -	[165]
Achromobacter xylosoxidans GYP4	2,2,4,4 -tetrabromodiphenyl ether (BDE-47)	pH = 4, Ci = 1 mg/L, t = 4 days, T = 30 °C, agitation speed = 150 rpm	90.8% -	[198]
Pseudomonas fluorescens	Pentachlorophenol	pH = 8.5, Ci = 250 mg/L, t = 7 days, T = 30 °C, agitation speed = 160 rpm	99.9% -	[199]
Janibacter sp. FAS23	Pentachlorophenol	pH = 6.9, Ci = 20 mg/L, t = 144 h, T = 30 °C	99.06% -	[167]
Bacillus cereus HWB1	4-Chlorophenol	pH = 7, Ci 4-chlorophenol = 150 mg/L, Ci 4-nitrophenol = 85 mg/L, t = 5 and 3 days, T = 30 °C, agitation speed = 150 rpm	100% -	[166]
	4-Nitrophenol		78% -	
Pseudomonas taiwanensis ECAe22	4-Chlorophenol	pH = 8.5, Ci 4-chlorophenol = 150 mg/L, Ci 4-nitrophenol = 85 mg/L, t = 5 and 3 days, T = 30 °C, agitation speed = 150 rpm	61% -	
	4-Nitrophenol		100% -	
Pseudomonas aeruginosa HS9	Hexabromocyclododecanes	pH = 8, Ci = 1.7mg/L, t = 14 days, T = 30 °C	69% -	[146]
Stenotrophomonas maltophilia OG2	Endosulfan	pH = 8, Ci = 100 mg/L, t = 10 days, T = 30 °C, agitation speed = 150 rpm	81.53% -	[151]
FUNGI				
Candida sp. VITJzN04	Lindane	pH = 7, Ci = 600 mg/L, t = 6 days, T = 30 °C, agitation speed 120 rpm	100% -	[174]
Rhodotorula sp. VITJzN03	Lindane	pH = 6, Ci = 600 mg/L, t = 10 days, T = 30 °C, agitation speed 120 rpm	100% -	[168]
Fusarium verticillioides AT-100	Lindane	pH = 7, Ci = 100 mg/L, t = 264 h, T = 30 ± 2 °C, agitation speed = 120 rpm	86% -	[148]
Mucor racemosus strain DDF	Dieldrin	Ci = 13.2 μM, t = 10 days, T = 25 °C	90% -	[195]
Mortierella sp. strain W8	α-endosulfan	Ci = 8.2 μM, t = 14 days, T = 25 °C	53.3% -	
	β-endosulfan		11.1% -	
Mortierella sp. strain Cm1-45	α-endosulfan		47.2% -	
	β-endosulfan		25.1% -	
Trichoderma viride	Dicofol	pH = 7, Ci = 100 mg/L, t = 28 days, T = 27 ± 1 °C	92% -	[184]
Trichoderma harzianum			96% -	

Penicillium chrysogenum	Endosulfan	pH = 5.6 ± 0.2, Ci = 10 mg/L, t = 35 days, T = 30 °C, agitation speed = 130 rpm	69.4%	[189]
			-	
Aspergillus flavus			72.3%	
			-	
Aspergillus niger			77.2%	
			-	
Rhodotorula sp. NS01	Benzo[a]pyrene	Ci = 10 mg/L, t = 7 days, T = 30 °C, agitation speed 120 rpm	52%	[200]
			-	
Candida tropicalis W1	4-chlorophenol	Ci = 150 mg/L, t = 20 h, T = 30 °C	100%	[201]
			-	
Lasiodiplodia theobromae	Benzo[a]pyrene	Ci = 100 mg/L, t = 10 days, T = 30 °C, agitation speed 150 rpm	53.0 ± 0.9%	[193]
			-	
Cunninghamella sp. UMAS SD12	Pentachlorophenol	pH = 5.5, Ci = 20 mg/L, t = 15 days, T = 28 °C	51.7%	[197]
			-	

Ci = initial concentration of POP in solution, t = contact time, T = temperature.

Table 5. Persistent organic pollutant removal by inactive microbial biomass.

Microorganism	POPs	Optimal Conditions	Efficiency/ Sorption Capacity	Ref.
Escherichia coli	Lindane	Ci = 4 mg/L, T = 20 °C, D = 4 g/L, t = 4 h, agitation speeed = 250 rpm	-	[140]
			0.5 mg/g	
Zoogloea ramigera			-	
			2.8 mg/g	
Bacillus megaterium			-	
			0.7 mg/g	
Bacillus subtilis			-	
			0.6 mg/g	
Emericella nidulans *Penicillium miczynskii*	2,4-Dichlorophenoxyacetic acid	Ci = 0.12,0.25,0.5 and 1 mM, T = 20 °C, D = 10 g/L, t = 3 h	70%	[144]
			-	
	2,4-Dichlorophenol		70%	
			-	
	4-Chlorophenol		50%	
			-	
130Rhizopus oryzae	Lindane	pH = 7, Ci = 0.1 mg/L, T = 18 °C, t = 250 min, D = 8 g/L, biomass age = 1–7 days	90.2%	[142]
			-	
		pH = 7, Ci = 200 μg/L, T = 30 °C, agitation speed = 120 rpm, t = 5h, D = 1.67 g/L, biomass age = 1–7 days	107.5 μg/g	[209]
			-	
Rhizopus arrhizu	Lindane	Ci = 1 mg/L, T = 20 °C, D = 4 g/L, t = 3 days, agitation speeed = 250 rpm	2.7 mg/g	[141]
			-	
	2-Chlorobiphenyl		11.1 mg/g	
			-	
	Pentachlorophenol		14.9 mg/g	
			-	
Mucor racemosus	Pentachloronitrobenzene	Ci = 250 mg/L, T = 21 °C, D = 10 g/L, t = 6 h, agitation speeed = 180 rpm	5.1 mg/g	[210]
			-	
Rhizopus arrhizus			4.6 mg/g	
			-	
Sporothrix cyanescens			2.6 mg/g	
			-	

Mycobacterium chlorophenolicum PCP-1	Pentachlorophenol	pH = 7, Ci = 50 mg/L, T = 30 °C, agitation speed = 120 rpm, t = 1.5 min, D = 0.12 g/L	~90 μmol/g -	[29]

Ci = initial concentration of POP in solution, t = contact time, T = temperature.

5. Key Considerations and Future Perspectives for Process Scale-up

The performance that various living or dead microorganism species have shown in removing of POPs and heavy metals makes them promising alternatives for removing of these types of pollutants from liquid media. Since in real media a consortium of microorganisms is available, some bioremediation studies [211] showed that the process is more efficient using simultaneous microbial strains instead of one single species. Advances in genetically modified microbes engineering, microbial fuel cells-based techniques, biofilm-mediated techniques suggest that bioremediation technologies would be very promising in the near future [212]. Biosorption potential has been performed at laboratory and pilot scales even using real wastewater effluents [20,213].

However, the majority of the studies are performed under laboratory conditions, and futher studies are needed to facilitate upscaling of lab scale options to industrial scale applications, considering both environmental and economic criteria. In spite of the fact that some commercial biosorbents are available for biosorption of HMs ions (e.g., AlgaSORB, Bio-Fix, B.V.SORBEX), there is no trend in adoption of biosorption as a wastewater treatment technology [214]. For further details on these biosorbents please see the paper of Kanamarlapudi et al. [214]. Previous to commercial application, biosorbents should fulfill some specific conditions in order to be optimum and standardized to different effluent type. The economic feasibility and the environmental impact in terms of large-scale application are necessary to be considered [214]. Also, an integrated approach for obtaining multiple energy as well as non-energy products, including biosorbents, can be developed for a more sustainable and profitable use of the microbial biomass. In this sense, the design of the scale-up processes can be carried out based on a similar flowsheet as the one described by Qamouche et al. [215].

In this regard, sustainable application of biosorption and bioaccumulation processes can be expanded on a larger scale requiring different mindset and new approaches. In research projects there is an increasingly demand in terms of sustainability dimension of new processes from the beginning stages (design phase, before implementation) [216]. The microbial process scale-up can be seen as a new perspective from the environmental impact evaluation point of view. In this regard, the use of microorganism for removal of environmental pollutants from contaminated media is considered an efficient and eco-friendly process [70].

Crater and Lievense [217] stated that "*in scaling up microbial processes, it is clearly impactful to get it right and to get it right the first time*". They also provided three guiding principles as a basis in scale up such as: start with the end in mind; be operose with details; be aware of the unexpected [217]. To save the risks of failure during process scale-up an important approach is the scientific part, which gives the opportunity to change any process and also reduces cost of implementation [218]. The scientific database comprises some analysis that can be used in the scale-up processes such us: life cycle assessment (LCA), life cycle costs (LCC) and social.

Life cycle assessment (LCA) analysis is widely used for processes or product systems at different development stages: for a process/product already developed, or at early design stage. In the scale-up process this analysis is defined as ex-ante LCA, due to the capacity of giving a potential impact of the new process before implementation [219]. The scale-up through LCA methodology follows three important steps [219] as represented in Figure 8.

As it was already mentioned, the scientific database is very important in this process, to identify the production scale and maturity of the production system, which is the first step in scale-up process. The scientific database collection started from the laboratory scale

studies where the chemical reaction behavior as well as temperature, pressure and other important parameters are determined [220]. In biosorption and bioaccumulation process some of these parameters are of high importance (as already was discussed in Sections 3.2 and 4.2).

In the second stage, the proposed system is described and defined for the LCA development. First, the life cycle impact (LCI) is elaborated, then the life cycle impact assessment (LCIA) is performed. The scale-up process is described in the last stage, based on a comparative analysis derived from LCA results. The third stage defines the most significant factors responsible for inconsistencies between laboratory scale and large scale, which can be adapted to the new scale [221].

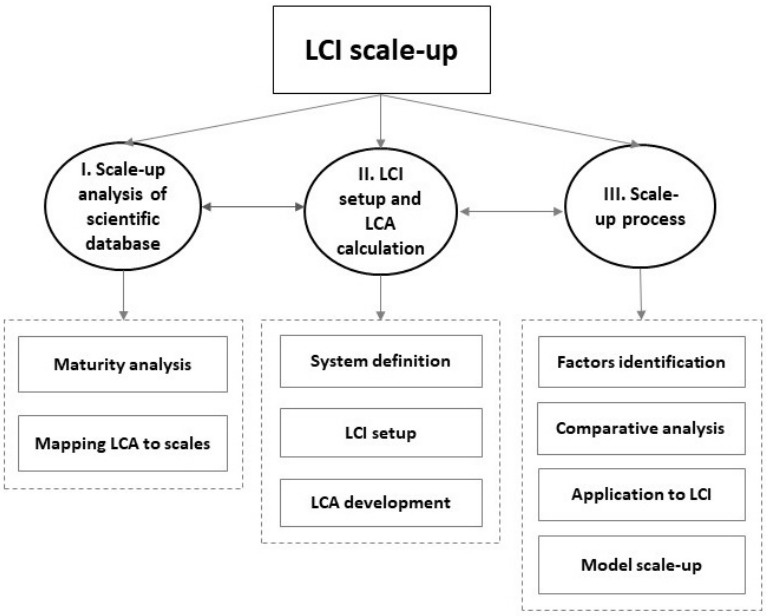

Figure 8. LCI scale-up methodology.

From our knowledge, the scale-up of microbial process is a quite new approach, especially in line with the environmental criteria. However, there are some studies that debate the scale-up concept from a laboratory scale to industrial one considering LCA approach. For example, Piccinno et al. [216] in their study analyzed the impact of a chemical process at industrial scale. They considered an advanced stage of the process (a pilot plant) to simulate a chemical process scale-up by using the same apparatus and connection in all the steps. They proposed five-steps for the scale-up framework to perform LCA analysis: laboratory protocol, plant flow chart considering scale and reactor size, separate scale-up of each process step and linkage of process steps. In conclusion, this approach was relatively simple and efficient to provide the potential impacts of chemical process at industrial level. Later, Crater and Lievense [217] proposed the scale-up of an industrial microbial processes, involving cultivation of microbes in bioreactors (fermentation). They started from the idea that scale-up should be realized in two phases to minimize the risk of full-scale manufacturing plant (capital investment), validation process, the supply chain and market demand. After analysis, some important key challenges for a successful scale-up were pointed out, namely that it is very important to have technical support during all phases and the laboratory or pilot plant has to be validated. According with Ghiron et al. [222], it is important to stress towards the potential of evaluating environmental feasibility of a new process based on lab and pilot-scale results.

6. Conclusions

The majority of HMs and POPs are very toxic to both human and environment. Water is one of the most important natural resource which is severely affected especially by anthropogenic pollution. Thus, different strategies are currently available for remediation of polluted-water bodies. Bioremediation is considered one of the most proper alternatives dealing with polluted sites. In this regard, a diversity of microbial strains proved to have an important potential to remove both heavy metals and persistent organic pollutants from liquid mediums. The potential of microorganisms to remove or reduce these contaminants lies first of all in the complex and diverse mechanisms involved at extracellular and intracellular level. Thus, in order to tolerate and remove the toxic pollutants, the microorganisms are able to transform POPs through co-metabolism, biomineralization, extracellular biodegradation and other mechanisms mediated by various enzymes and substances secreted by cells. By reduction, oxidation, hydrolysis, dehalogenation and methylation reactions catalyzed by enzymes, the POPs lead to a complete or partial mineralization. The results of these reactions consist in a wide variety of metabolites less complex and less toxic, CO_2 and energy. In case of the removal of HMs, the main mechanisms involved are biosorption, bioaccumulation, biotransformation, bioprecipitation, metal reduction, proton volatilization release, biomethylation, and chelation by ionic and covalent interaction. An important role is also played by the synthesis of the extracellular polymeric substances, which facilitate these processes.

Biosorption (a passive mechanism) has been shown to be generally a rapid process and to provide a better sorption capacity compared to bioaccumulation (active mechanism). Biosorption process depends on several experimental conditions (temperature, pH, contact time and agitation speed), pollutant type and its initial concentration and other factors.

Although important progress has been made in selecting the proper microorganisms for the decontamination of polluted waters, some issues still need to be addressed. For example, microbial genetic engineering proved to increase the capacity of microorganism to tolerate and accumulate HMs. Moreover, immobilizations of microbial biomass in polymeric matrixes may increase its capacity and resistance to chemicals or may provide better mechanical strength and optimum porosity.

The feasibility of the process at large scale is still not fully demonstrated and nowadays, there is no trend in adoption of biosorption in current wastewater treatment practice. Further studies are needed to demonstrate the technological feasibility and environmental performance at large scale application. In this regard, a sustainable scale-up process should be considered by applying LCA methodology which is a new approach that should be used in the evaluation of the commercial up-scaling of biosorption and bioaccumulation processes considered for the remediation of polluted-water bodies. In the scale-up process this analysis is defined as ex-ante LCA, due to the capacity of giving a potential impact of the new process before implementation. Finally, for a sustainable scale-up it is necessary to consider all the necessary data starting from the design phase to the end of the process for a potential expansion in the near future.

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