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BIOSORBENTS BASED ON MICROORGANISMS

ΒY

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Abstract. Biosorption is a technique used for the removal of not easily biodegradable pollutants from waters (especially metals and dyes), that can use a variety of biomaterials with adsorptive properties including microbial microorganism (algae, bacteria, fungi), but also industrial and agricultural wastes. The biosorption abilities of microbial biomass towards dyes and metal ions have been extensively studied, as these biosorbents are low-cost and ecofriendly materials for water/wastewater treatment applications, and can be chemically modified, via various techniques, or genetically engineered to enhance their biosorption capacity. The functional groups, such as carboxyl, amine and phosphonate of the cell wall constituents (peptidoglycan, manan, chitin and chitosan), offer increase biosorption potentials.

Keywords: biosorption; dyes; immobilization; metals ions; microbial biosorbents; wastewaters.

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1. Introduction

Nowadays, ecological problems are connected with the demographic explosion and with high industrialization; also, the reduction of natural resources together with the increase of wastes quantity, decrease of soil fertility, chemical pollution of environment and degradation of ozone layer of our planet. Alarming is the fact that high risk ecological compounds which have very complex structures and compositions are present in very small quantities (μ g), are not biodegradable and are characterized by toxic cumulative action in time.

Water is an important factor in all ecological balances, and its pollution is a current problem with serious consequences on the population health, as it affects the quality of life on a global scale.

Water pollution, caused by heavy metals, is a global priority. High amounts of metals are released into the environment as a consequence of both industrial activities (mining industry, metallurgy, thermal and power plants), and non-anthropogenic sources such as: erosion phenomena and volcanic eruptions and can directly or indirectly affect human health (through the food chain, food ingestion, water consumption).

Metals, in small amounts, are essential elements for living organisms (as cofactors for different enzymes) but, at high concentrations, they can be toxic and therefore need to be removed from the environment. Among the conventional methods of wastewater treatment with metals are included: membrane processes (reverse osmosis, electrophoresis); microfiltration, chemical precipitation, ion exchange, adsorption onto active coal/carbon. Of these, some impose relatively high costs and can generate large amounts of chemical waste. Formation of metal species with low solubility or complexation of some metals with organic compounds (generating compounds more toxic than the original form) sometimes complicates the purification processes of liquid flows.

The presence of dyes in wastewater or surface water raises both aesthetic problems, preventing the penetration of light and contamination with organic products resulting from the decomposition of these dyes, compounds that have cumulative toxic action over time, are carcinogenic or mutagenic (Lellis *et al.*, 2019; Zaharia and Şuteu, 2012).

The scientific literature presents a lot of *physical, chemical and physico-chemical* methods frequently applied in water depollution (precipitation, coagulation–flocculation, oxidation, reduction, ion exchange, membrane filtration, adsorption with charcoal or polymeric materials, electrochemical treatments, inverse osmosis, recuperation by evaporation, solvent extraction, etc.) (Forgacs and Cserháti, 2004; Zaharia and Şuteu, 2012; Ahmad *et al.*, 2015; Ruan *et al.*, 2019; Bhatia *et al.*, 2017; Hasanpour and Hatami, 2020; Azimi *et al.*, 2020; Tara *et al.*, 2020; Beulah and Muthukumaran, 2020), characterized by production of sludge and other toxic wastes (supplementary costs for processing and

transformation in products without risks for receiving environment). For the minimization of all these disadvantages, the researchers have been directed toward techniques with special sensibility and selectivity, that are not subdue to matrix effects, and permit the concomitant achievement of concentration and proper determination. These aspects made possible the re-direction of researches toward application of different *biotechnological procedures for wastewater treatment* and promotion of the most advanced bioprocesses in order to minimize and even eliminate the negative effects of pollutants. The main target would be to increase the depollution processes efficiency together with the consistent reduction of the cost for energy and manual labor, the volume decreases of manipulated raw materials, elimination of any pollution sources and no secondary production of dangerous wastes.

These include, among others biosorption which became an alternative to conventional wastewater treatment methods, being an environment - friendly and cost - effective technique, that uses dead microbial biomass (bacteria, fungi, algae and plants) for the removal of metal ions (inorganic water pollutants) or pharmaceutical and dyes (organic water pollutants) from aqueous solutions/wastewaters.

Biosorption is characterized mainly by: low cost, elimination of ecological risk of the toxic compounds recovery, the possibility to treat large volumes of effluents with low concentrations of pollutants. Natural support, generated by plants, mushrooms, seaweed, microorganisms from soil or water is biodegradable and can be integrated in carbon cycles being also compatible with self-control environmental processes (Park *et al.*, 2010; Şuteu *et al.*, 2012; Suteu *et al.*, 2013a; Michalak *et al.*, 2013; de Freitas *et al.*, 2019; Agarwal *et al.*, 2020). Microorganisms are capable of tolerating unfavourable circumstances, through mechanisms that evolved for millions of years, giving them the ability to tolerate extremely harsh conditions (Mustapha and Halimoon, 2015; Velkova *et al.*, 2018), their use for the passive uptake of contaminants in dead/inactive forms received much attention in recent years.

The aim of this paper is to systematize the data from the literature regarding the use of microorganisms as biosorbents and to present and characterize some biomass obtained in the laboratory for use in biosorption processes.

2. Microbial Biosorbents

The use of microorganisms in biosorption is one of the most promising ways to remove heavy metal ions or organic pollutant such as dyes from contaminated water, due to their high removal efficiency, low cost, and simplicity in application (Vijayaraghavan *et al.*, 2008; Todorova *et al.*, 2019; Adewuyi, 2020). Through biosorption, the contaminants are bound to the surface of microorganisms through chemical interactions, similarly to a chemical ion exchange material and separated from the liquid stream.

Biosorbents for the removal of metals/dyes mainly come under the following categories: microbial cells (bacteria, fungi, algae), industrial and agricultural wastes, and other polysaccharide materials (Busi *et al.*, 2016) Residual biomasses from industrial processes (food/pharmaceutical industries) have been used as biosorbent for efficient accumulation of heavy metals, as they are generated as waste, which can be attained free or at low cost from industry.

The external layer of bacterial biomass is the cell walls that contain especially peptidoglycan, proteins and lipids with functional groups such as carboxyl, sulphate, phosphate that can bind contaminants. However, the cell wall composition is different between the two main classes of Bacteria: Gram positive and Gram negative: Gram-positive bacteria are constituted of a thick layer composed of peptidoglycan, with increased rigidity and stability, while Gram-negative bacteria have a thin layer of peptidoglycan and more phospholipids, increasing its fragility. The capacity to adsorb contaminants can be further increase by applying different techniques that would increase the available number of binding groups: drying at high temperature (*e.g.* 80° C), alkali or acid treatment. The anionic groups as: phosphoryl, carbonyl, sulfhydryl and hydroxyl greatly enhance the biosorption process efficiency.

In contrast, the cell walls of fungi has a different composition: polysaccharides β -1,3 glucan, β -1,6 glucan, mannan-binding protein, glycoproteins, chitin and chitosan, lipids, that possess chemical groups as: acetamido, amide, phosphate, amino, amine, sulfhydryl, carboxyl and hydroxyl available for biosorption.

Free microbial biosorbents have often low density, small size, low mechanical stability and elasticity (difficult desorption, separation and regeneration) that could be overcome by biomass immobilisation (offering the possibility of continuous biosorbent processes) on suitable carriers (Velkova *et al.*, 2018).

2.1. Heavy Metal Biosorption

Potent metal biosorbents under the class of bacteria and fungi are presented in Table 1.

The biosorption efficiency depends not only on the type of metal ions, but also on the microbial type (due to variations in the cellular constituents) and on the pre-treatment or immobilization technique used for the biomass (Aryal, 2020; Mustapha and Halimoon, 2015; Roy *et al.*, 2018; Todorova *et al.*, 2019).

The optimum conditions for heavy metal biosorption imply usually:

• Weak acidic pH (due the involvement of carboxyl and other acidic functional groups that bind the metal cations through various mechanisms), however pH above 5 was reported as optimum for the metal biosorption in yeast cells (Shamim, 2017);

• Short contact times (sufficient to reach steady state for metal-bacterial biomass system);

• Gram positive bacteria due to presence of glycoproteins are more efficient biosorbents compared to Gram negative bacteria (due to more phospholipids and less peptidoglycan from the cell wall);

• Biosorption ability of microbial cells can be manipulated by physical treatments, including heat processes (autoclaving) or chemical treatments including the use of dimethyl sulfoxide, detergents, orthophosphoric acid, formaldehyde, gluteraldehyde, NaOH.

No	Microorganisms	Metal	Uptake,	Reference
	6	removed	mg/g	
1	Bacillus licheniformis	Chromium	69.4	(Zhou et al., 2007)
2	Pseudomonas sp.	(VI)	95.0	(Ziagova et al., 2007)
3	Staphylococcus xylosus		143.0	(Ziagova et al., 2007)
4	Arthrobacter viscosus		13.0	(Silva et al., 2012)
5	Paecilomyces lilacinus		189.13	(Sharma and Adholeya,
				2011)
6	Penicillium griseofulvum		75.1	(Abigail et al., 2015)
7	Bacillus sp. (ATS-1)	Copper	16.3	(Tunali et al., 2006)
8	Pseudomonas putida		96.9	(Uslu and Tanyol,
				2006)
9	B. thuringiensis OSM29		39.84	(Oves et al., 2013)
10	Ochrobactrum MT180101		-	(Peng et al., 2019)
11	Bacillus cereus		50.32	(Babak et al., 2012)
12	Pseudomonas sp.	Cadmium	278.0	(Ziagova et al., 2007)
13	Enterobacter sp. J1		46.2	(Quintelas et al., 2009)
14	Stenotrophomonas maltophilia		0.12	(Congeevaram <i>et al.</i> , 2007)
15	Staphylococcus xylosus		250.0	(Ziagova <i>et al.</i> , 2007)
16	Bacillus sp. (ATS-1)	Lead	92.3	(Tunali <i>et al.</i> , 2006)
17	Pseudomonas putida		270.4	(Uslu and Tanyol,
	X			2006)
18	Enterobacter cloacae		67.9	(Rani et al., 2010)
19	Bacillus cereus		36.71	(Babak et al., 2012)
20	Geobacillus thermodenitrificans		53	(Samarth et al., 2012)
21	Bacillus sp.	Mercury	7.9	(Green-Ruiz, 2006)
22	Enterobacter cloacae	-	43.23	(Rani et al., 2010)
23	Saccharomyces cerevisiae		64.2	(Mustapha and
				Halimoon, 2015)
24	Phosphorylated Saccharomyces	Cu ²⁺	68.58	(Ojima et al., 2019)
	cerevisiae	Zn^{2+}	76.4	
		Pb^{2+}	188.37	
		Cd^{2+}	98.91	
25	Aspergillus versicolor	Fe (II)	22.25	(Hassouna et al., 2018)

Table 1Examples of Various Microbial Species Used for Metal Biosorption

2.1. Dye Biosorption

Microbial biomass is known to effectively remove soluble toxic organic substances as dyes by biosorption, due to the presence of various functional groups on the microbial surface. Biosorption can bind the dyes from a waste solution by complexation, chelation, precipitation, and ionic interactions (Argun *et al.*, 2017; Lellis *et al.*, 2019; Kabbout and Taha, 2014; Kumar *et al.*, 2015). Eukaryotic cells, especially fungi and yeasts were used for the removal of azo dyes from the textile wastewater's colour, through the cell wall that is considered to be the primary site of biosorption. Biosorption depends upon the initial dye concentration, pH of the aqueous solution, temperature, and biomass dosage.

In Table 2, several examples on dye removal by microbial biomass is given.

NL	Examples of various Microbial Species Osed for Dye Blosorphion					
INO	Microorganism	Dye removed	Uptake	Reference		
1	Aspergillus parasiticus	Reactive red 198	1.03×10^{-4}	(Akar <i>et al.</i> ,		
			mol/g	2009)		
2	Aspergillus fumigates	Methylene blue	93%	(Abdallah and		
				Taha, 2012)		
3	Streptomyces rimosus		34.3 mg/g	(Nacèra and		
				Aicha, 2006)		
4	Corynebacterium	Reactive black 5	419.0 mg/g	(Vijayaraghavan		
	glutamicum			and Yun, 2007)		
5	Corynebacterium	Reactive blue 4	173.1 mg/g	(Han and Yun,		
	glutamicum			2007)		
6	Kluyveromyces	Remazol Black B	37 mg/g	(Meehan et al.,		
	marxianus IMB3			2000)		
7	Lentinus concinnus	Reactive Yellow 86	190.2 mg/g	(Bayramoğlu and		
			00	Yilmaz, 2018)		
8	Saccharomyces	Brilliant Red	104.167	(Şuteu et al.,		
	cerevisiae	HE-3B	mg/g	2013b)		
9	Lentinus concinnus	Disperse Red 60	65.7 mg/g	(Bayramoğlu et		
		-	00	al., 2017)		

 Table 2

 Examples of Various Microbial Spacies Used for Due Rieserption

Analysing the biosorption efficiency, acidic pH was found to be favourable for dye removal: *Saccharomyces cerevisiae* showed maximum sorption at pH 6.0, while *Aspergillus niger* has been effectively utilized as a biosorbent at pH 5.0 (Shamim, 2017).

3. Biomass Immobilization

Despite the fact that many types of biomass demonstrate higher sorption capacities than conventional sorbents, for example, ion-exchange resins, their use is limited due to physical problems. Multiple microorganisms demonstrated high sorption capacities compared to conventional sorbents (ion-exchange resins). However, their use is limited due to physical problems, which can be solved by immobilization, obtaining particles with good physico-chemical stability (higher mechanical resistance). Several problems need to be considered when choosing a proper immobilization technique, as immobilisation implies supplementary cost, the contaminant diffusion through the support that increases time and decreases the process efficiency, and lowers the biosorbent capacity due to interaction between the support and the active sites of the biosorbent.

Immobilization on various supports improves microorganism's properties: stability, thermal and pH resistance, handling facilitation, easy cell separation from the liquid medium. Immobilization techniques can be divided into two groups (Galaction *et al.*, 2011; Girijan and Kumar, 2019; Moreno-Garrido, 2008; Rani and Kaushik, 2014):

(1) passive – based on the film forming property of the microorganism. Support materials are introduced prior to sterilization and inoculation with starter culture and are left inside the continuous culture for a period of time, after which a film of microorganisms is apparent on the support surfaces. This technique offers advantages over other methods of immobilization, including ease of immobilization (natural entrapment), no need for chemical addition, large mass transfer rate in the particles, and ease of scale-up of the immobilization technique. However, this technique can be only applied to microorganisms showing natural tendency to attach or aggregate on solid support.

(2) active – based on gel entrapment and chemical attachment (covalent binding to vector compounds and cross-linking) should be distinguished. Gel entrapment is the most widely used technique for microorganism immobilization, carried out using natural polysaccharides (chitosan, agars, carrageenans or alginates), proteins (gelatin, collagen) or synthetic polymers (acrylamide, photocrosslinkable resins, polyurethanes). Chemical attachment presents some great disadvantages when microorganisms are intended to be immobilized, because the chemical interaction (covalent bonding or cross-linking – involving glutaraldehyde or, or photocrosslinkable resins) induces cell surface damages. These immobilization techniques are presented in Fig. 1:



Fig. 1 – Technics used for microbial immobilisation.

In Table 3 the applications of immobilized biomass are presented for different contaminants.

Biosorbent	Chemical species	Reference
Biosorbent	removed	Reference
Immobilized <i>Desmodesmus sp.</i> in	Methylene blue	(Al-Fawwaz and
sodium alginate	Malachite green	Abdullah, 2016)
Immobilized bacillus subtilis in	Methylene blue	(Ganta et al., 2016)
calcium alginate		
Lentinus concinnus immobilized in	Reactive Yellow	(Bayramoğlu and
polyvinyl alcohol/polyethyleneoxide	86	Yilmaz, 2018)
hydrogels		
Immobilized biomass of strains of	Brilliant green and	(Przysta´s <i>et al.</i> ,
fungi (<i>Pleurotus ostreatus</i> – BWPH,	Evans blue	2018
<i>Gleophyllum odoratum</i> – DCa and		
<i>Poly-porus picipes</i> – KWP1/) on the		
supports		
<i>Bacillus subtilis sp</i> immobilized in	Brilliant Red HE-	(Horcin $at al = 2020$)
sodium alginate	3B	(1101010 07 07., 2020)
Non-living <i>Bacillus sp.</i> and		(Horciu <i>et al.</i> , 2019)
Aspergillus sp. biomass immobilized		()
in alginate		
Saccharomyces cerevisiae	Orange 16,	(Horciu et al., 2018)
immobilized in alginate	Brilliant Red HE-	
	3B, Rhodamine B,	
	Methylene Blue	
Lentinus concinnus biomass was	Disperse Red 60	(Bayramoğlu <i>et al.</i> ,
immobilized to carboxyl derivative		2017)
of cellulose, carboxymethyl cellulose	Dh(II) Cd(II) and	(Tedenson et al
Bacillus cereus immobilized in	$PD(II), Cd(II) and U_{\alpha}(II)$	(1000rova et al., 2010)
with activated carbon or with	ng(II)	2019)
bentonite into alginate gel		
Dead cyanobacterial biomass of	Cr(VI), Co (II)	(Rani and Kaushik.
<i>Nostoclinck</i> immobilized in different		2014)
matrices like calcium alginate,		, ,
polyvinyl alcohol alginate and		
polyvinyl alcohol alginate		
glutaraldehyde		

Table 3Examples of Various Microbial Species Immobilized Used as Biosorbents

One immobilisation technique applied for residual biomass is entrapment in calcium alginate beads (*Sacharomyces cerevisiae* and *Bacillus sp.* were entrapped by drop-wise addition of an aqueous mixture of biomass and

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sodium alginate to a solution with hardening effect - calcium chloride – Fig. 2) (Galaction *et al.*, 2011).

Biomass	Saccharomyces cerevisiae	Aspergillus sp.	Bacillus sp.			
Powder of bior	nass					
Forming the Suspension in alginate						
Biomass granules immobilized in alginate		s-hote levels a				
Granules after dye biosorption						

Fig. 2 – Immobilised some type of microorganisms for dye (Brilliant Red HE-3B and Methylene Blue) biosorption.

Alginate is non-toxic and non-pathogenic, is not expensive and readily available, with high water affinity and ability to form gels. The use of residual biomass also adds several advantages: low cost, no necessity for nutrient medium and maintenance of pure microbial cultures, high sorption and desorption rate in wide pH range, use of non-complicated equipment. However, the biosorption using immobilized microbial biomass has been studied especially at laboratory scale (batch and column).

4. Conclusions

Microbial biomasses have different biosorptive abilities, variable within each taxonomic group, which can be increased by physical and/or chemical pre-treatment and improved through operational conditions.

In order to have a successful application of biosorption with industrial applications several problems need to be solved. Among them the selection of adequate biomass, with high biosorption capacity and selectivity (increased through chemical or physical modification or immobilisation) and low cost is very important. For use with real industrial effluents the working parameters (temperature, pH, biosorbent concentration, water quality, different modes of operation) optimisation is necessary.

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BIOSORBENȚI PE BAZĂ DE MICROORGANISME

(Rezumat)

Biosorbția este o tehnică utilizată pentru îndepărtarea poluanților nebiodegradabili din ape (în special metale și coloranți), care poate utiliza o varietate de biomateriale cu proprietăți adsorbante, inclusiv microorganisme (alge, bacterii, ciuperci), dar și deșeuri industriale și agricole. Abilitățile de reținere ale biomasei microbiene față de coloranți și ioni metalici au fost studiate pe larg, deoarece acești biosorbenți sunt materiale ieftine și ecologice pentru aplicarea în procese de tratare a apei / apelor uzate și pot fi modificați chimic, prin diferite tehnici, sau modificări genetice pentru a le îmbunătăți capacitatea de biosorbție. Grupările funcționale, cum ar fi carboxil, amină și fosfonat ale constituenților peretelui celular (peptidoglican, manan, chitină și chitosan), oferă potențiale de biosorbție crescute.