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Dedicated to the memory of
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RECENT ADVANCES IN BIOSORPTION OF HEAVY METALS: SUPPORT TOOLS FOR BIOSORPTION EQUILIBRIUM, KINETICS AND MECHANISM

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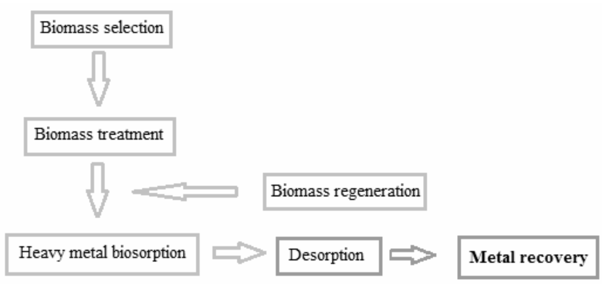
Heavy metals are increasingly present in industrial wastes and effluents, which can generate serious concerns for environmental quality and human health. Consequently, there is a continuous expansion of researches for new approaches and developments to guarantee environmental cleaning-up. Although there are some physico-chemical established methods for the removal of heavy metals from various environmental compartments, biosorption gains further confidence as a reliable alternative compared to classical technologies, which are expensive and sometimes unreliable. This paper aims to analyze the biosorption as a biotechnological strategy for the decontamination of aqueous effluents containing heavy metal ions, in terms of its potential for metal immobilization and uptake. The paper also focuses on the most important parameters affecting the removal of heavy metals by various categories of biosorbents – both living and non-living forms of biomass – and provides new alternatives for modeling and optimization of process equilibrium and kinetics. A special attention was paid to biosorption mechanism, as a factual challenge for process optimization and scale-up. The potential benefits and problems associated to metal removal by biosorption are highlighted.



INTRODUCTION

The pollution with heavy metals has become one of the most serious environmental problems of today. Considering the toxic effects of heavy metals on human health and on various forms of life, the industries are advised to systematically treat the wastewaters to minimize and/or remove the metal ion contents.[1-3] Some of the most important heavy metals considered as priority due to their high toxicity, prevalence and persistence in the environment are lead (Pb), mercury (Hg),

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cadmium (Cd), chromium (Cr) and arsenic (As).[4-6] There are some works which summarized the main aspects related to heavy metals toxicity and human health hazards associated with their presence in the environment.[7-10]

The need for a full understanding of the toxic effects caused by release of heavy metals into the environment and for including more severe environmental protection laws have encouraged studies on heavy metals removal and/or recovery from aqueous solution using certain eco-friendly, economic and low-tech treatment methods.[7] A literature survey shows that treatment technologies for heavy metal contaminated wastewater can be grouped into three categories:[4, 11] (1) chemical methods, such as chemical precipitation, chemical reduction and electrolysis; (2) sorption, enrichment, separation processes for metal removal without alteration of metal state, e.g. active carbon adsorption, extraction, ion exchange, reverse osmosis, electro dialysis, evaporation, etc.; (3) biological processes with adsorption, accumulation and enrichment mechanisms for metal removal, *e.g.* biosorption, bioflocculation, constructed wetlands etc. The removal of heavy metals from wastewaters before their discharge into the environment is usually achieved by applying a variety of physico-chemical processes (chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation, electrochemical methods). Although their performances are usually acceptable, these methods are not very efficient in treating heavy metals that have concentrations ranging from several to few hundred mg/L.[6, 12-14] Sorption is one of the few alternatives available for the removal of heavy metals with low concentrations in aqueous effluents.[15-17] Activated carbon, activated alumina or polymer resins which are sometimes non-regenerable and expensive materials, are the sorbents frequently applied for this purpose.[18] Studies and researches conducted in laboratory demonstrated that biosorption is a promising and cost-effective technology for the removal of heavy metals from aqueous solutions. In biosorption, biomass (non-living or living) or biopolymers are engaged as sorbents to sequester heavy metals from aqueous solutions.[13]

Biosorption is a process for rapid and reversible binding of metal ions from aqueous solutions onto functional groups that are present on the surface of biomass. It does not require high capital investments, while the operating costs are reasonable.[19] Because of these advantages, extensive researches exploring appropriate biosorbents able to effectively remove heavy metals from aqueous solutions were conducted during the past 20 years.[17, 20-21] A wide variety of biosorbents were employed as heavy metals sequestrants such as lignocellulosic materials, active or inactive microorganisms (e.g. fungi, yeast, bacteria), algae, waste biomass. The potential of these biomaterials for biosorption of heavy metals can be evaluated during batch or continuous flow column studies performed simultaneously with studies for the elucidation of metal-binding mechanisms.[22-24]

In this context, in this paper we elaborated an analysis of the biosorption of heavy metals considering the most relevant and effective biosorbent categories – as organic materials, along with a detailed description on factors affecting the biosorption process. Moreover, new updates on equilibrium and kinetics modeling and simulation tools are provided, while some recent advances in biosorption mechanism are discussed.

BIOSORBENTS

One of the major challenges for the researchers working in the field of biosorption relies in the identification of those biosorbents with sufficiently high metal-binding capacities and selectivity for heavy metals, for further application in full-scale processes. The biomass selection can be done from a large spectrum of easily available and low-cost biomaterials. Biosorbents used for biosorption purposes can be classified into three wide categories: (1) exopolysaccharides; (2) living cultures; (3) non-living biomass and preparations.[25] In order to enhance their performance and/or suitability for process applications, these biomaterials can be chemically pretreated.[17, 20, 21, 26, 27]

Laboratory experiments focusing on dead and/or living microorganisms capable to bind all kinds of heavy metals, can offer a good option to conventional adsorbents. The application of dead biomass for metal binding is usually considered of higher interest than the living biomass, which could be subjected to toxic actions of heavy metals, and requires the addition of nutrients and the monitoring of Biochemical Oxygen Demand and Chemical Oxygen Demand in solution. Therefore, dead cells (found sometimes in waste effluents from food industries) are low-cost and involve less care and maintenance.[28] Several other biosorbents such as algae, industrial or agricultural wastes, and other biomass categories behaved well in sequestration of different heavy metal ions. Some types of biosorbents can bind a broad range of heavy metals, while other biosorbents are specific for certain types of metals.[29-30]

Lignocellulosic wastes

At present, the concern for the use of cheap alternative biomaterials in the biosorption process has increased. The biosorption potential of lignocellulosic materials (either natural substances or agro-industrial wastes and by-products) was investigated by many researchers as an economic and eco-friendly alternative to other biomaterials.[1, 31-32] Lignocellulosics are abundant, inexpensive and renewable, possessing natural sorption ability. Also lignocellulosics with sorbed heavy metals can be reused in making fiber board. If natural fibers would replace the conventional synthetic materials, a possible pollution or disposal problem can be eliminated.[33-35] Agricultural wastes, especially those with a high percentage of cellulose, show a high potential for metal uptake. Thus, diverse agro-wastes have been successfully used to remove toxic heavy metals like Cd(II), Pb(II), Hg(II), Cu(II), Ni(II), Zn(II), Cr(III), and Cr(VI) from contaminated industrial and municipal wastewaters.[31] The functional groups such as acetamido, alcoholic, carbonyl, phenolic, amido, amino and sulphydryl groups present in agricultural waste biomass form metal complexes or chelates with heavy metal ions.[36] Table 1 presents a short summary on several types of lignocellulosic materials applied for the removal of heavy metals from wastewaters.

Microorganisms

A great amount of microorganisms belonging to various groups, e.g. bacteria, fungi, yeasts, cyanobacteria have been reported to bind a variety of heavy metals to different extents.[7, 48] There are several pathways in which the microorganisms remove metal ions from aqueous solution: (i) extracellular accumulation/precipitation, (ii) cell surface sorption or complexation and (iii) intracellular accumulation. Among these, process (ii) can occur, whether the organism is living or dead; process (i) may be facilitated by microbial viability while process (iii) requires microbial activity. Table 2 presents various combinations of microorganisms-heavy metals in wastewater treatment.

Table 1

Use of agricultural wastes and by-products for the removal of heavy metals in batch system

Metal ion	Biosorbent type	pH	Time (min)	Temperature (°C)	Removal efficiency (%)	Uptake (mg/g)	References
Cd(II)	Mustard	5.5	30	25	80	33.56	37
Cu(II)	Peanut shells	6.2	22	-	94.97	-	38
Cu(II)	*Pinus silvestris*	5	120	20	-	21.47	39
Cr(III)		5	120	20	31.41	39.63	
Cu(II)	Almond shells	5.6	2880	40	-	6.783	40
Cr(VI)	Sphagnum peat moss	1	1440	20	99	13.05	41
Cd(II)	Coir pith	-	-	-	-	18.72	42
Cu(II)	Cashew nut shell	5	30	30	82.11	20.09	43
Ni(II)	*Sphagnum* peat moss	6	1440	28	97.46	4.44	44
Zn(II)	*Sphagnum* peat moss	5	30	-	-	12.56	45
Cd(II)	Bael tree leaf	6	30	30	93.56	1.890	46
Pb(II)	Olive tree pruning	5	120	25	-	26.24	47

Table 2

Use of microorganisms for the removal of heavy metals in batch system

Metal ion	Biosorbent type	pH	Time (min)	Temperature (°C)	Removal efficiency (%)	Uptake (mg/g)	References
As(III)	*Rhodococcus* sp. WB-12	7	30	30	88.4	77.3	49
Cd(II)	Filamentous fungus, XJ-1	5	240	28	-	76.93	50

Table 2 (continued)

Cr(VI)	*Bacillus* sp. FM1	3	60	37	-	64.102	51
Cu(II)		5	60	37	-	78.125	
Cr(VI)	*S. cerevisiae*	2	2880	25	100	-	52
Cd(II)	*S. cerevisiae*	6	1440	40	86	12	53
Cr(VI)	*Phanerochaete chrysosporium*	6	-	-	81.47	-	54
Cr(III)	*Pleurotus ostreatus*	5.5	2880	25	-	108	55
Pb(II)	*Streptomyces* sp.	3	-	-	-	116	56
Pb(II)	*S. cerevisiae*	5	90	25	48.6	-	57
Zn(II)	*Acinetobacter* sp.	6	25	90	-	36	58
Zn(II)	Immobilized *C. utilis*	5.17	240	45	-	181.7	59
Cd(II)	*Agaricus bisporus*	5.5	240	25	76.10	3.49	60

Algae

Algae as a renewable natural biomass plentiful all over the world in the littoral zones have drawn the attention of researchers as new adsorbents for heavy metal removal. Several advantages in applying algae as biosorbents include the wide availability, low cost, high metal sorption capacity and reasonably regular quality.[61-63] About three million tons of seaweeds are harvested annually for food and algal products (*e.g.* agar, alginate, and carrageenan). The cell walls of algae generally contain three components: cellulose (as structural support), alginic acid, polymers (*e.g.*, mannuronic and guluronic acids) complexed with light metals such as sodium, potassium, magnesium and calcium, and polysaccharides (*e.g.*, sulfated).[13] Biosorption using algal biomass as a bio-based technology is therefore recognized as one of the most effective solutions for heavy metals removal from the environment. Table 3 summarizes the results of several studies on heavy metals removal from aqueous solutions by different types of algal biomass in batch system.

FACTORS AFFECTING THE BIOSORPTION PROCESS

For full understanding of biosorption potential, the analysis of all factors influencing the process is of high importance. The most important factors that should be taken into account when considering biosorption are: (i) the type and nature of the biomass; (ii) initial solute concentration; (iii) biomass concentration (biosorbent dosage/solution volume) in solution; (iv) physicochemical factors like temperature, pH, ionic strength.

Table 3

Use of algae for the removal of heavy metals in batch system

Metal ion	Biosorbent type	pH	Time (min)	Temperature (°C)	Removal efficiency (%)	Uptake (mg/g)	References
Hg(II)	*Sargassum* sp.	5	90	22	49.1	145.8	30
	Turbinaria conoides	5	90	22	58.1	170.3	
	Ulva sp.	5	90	22	42.5	138.4	
Cr(VI)	*S. marginatum*	1	70	27	55	32.63	64
	N. zanardinii	1	90	27	55	32.72	
Cd(II)	*Fucus vesiculosus*	-	250	8	98	-	65
Cd(II)	*Ulva lactuca* sp.	5	90	20	85	35.72	66
Pb(II)	*Ulva lactuca* sp	5	120	20	97	53.66	67
Cd(II)	*Anabaena sphaerica*	5.5	60	25	94.3	111.1	68
Cu(II)	*Chlamydomonas reinhardtii*	6	100	30	55	0.15	69
Cu(II)	*Spirulina platensis*	7	90	37	90.6	-	61
Cr(VI)	*Laminaria digitata*	2.5	2880	20	100	-	70

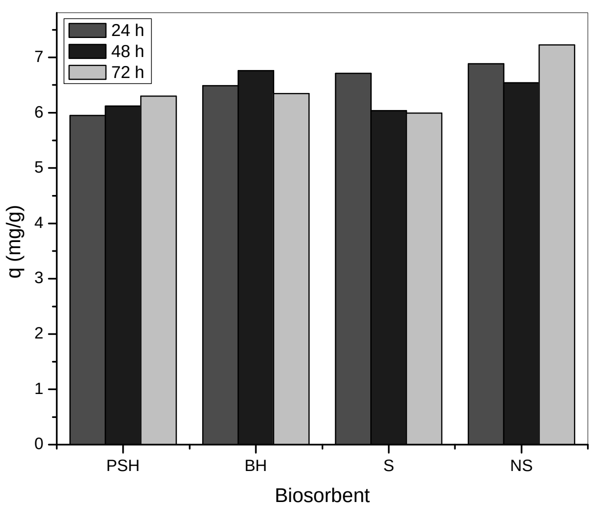
Usually, in literature, it is considered that the biosorption process can often occur under the following conditions:[71-72]
(a) in a certain interval, the temperature can have a negative or positive effect on biosorption;
(b) the pH of solution is a very important parameter of the process, since it influences the metal chemical speciation and solubility, the activity of biomass functional groups (active sites), and the metallic ion competition for active sites;
(c) in diluted solutions, the biomass concentration influences the biosorption capacity: at lower concentrations, there is an increase in the biosorption capacity;
(d) in solutions with different metallic species there is a competition among metals to occupy active sites.

In the work of Bulgariu *et al.*,[44] nickel(II) removal from aqueous solution onto peat moss was studied as a function of its initial concentration, under optimum conditions. The authors observed that a good efficiency of nickel(II) removal is obtained at a relative low concentration (below 90 mg/L), when nickel(II) concentration from residual solutions is lower than the permissible limits, making the peat moss an efficient adsorbent for wastewater treatment.

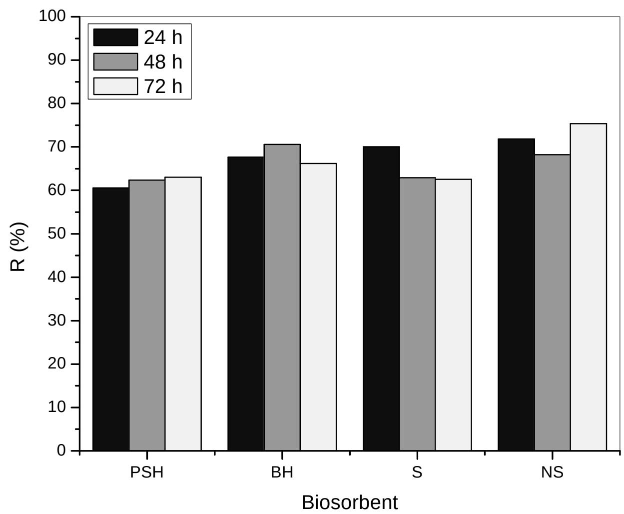
For example, some preliminary studies performed in our group on Cd(II) biosorption by different agricultural wastes revealed that nutshells have a higher removal capacity when compared with pumpkin seed hulls, bean hulls and straws (Fig. 1).

Effect of solution pH on biosorption performance

The pH value of aqueous solution can be considered among the most important physico-chemical factors influencing the biosorption process. It determines the speciation and solubility of metal ions and the charges on the sorption sites on biosorbent surface. Therefore, the ionic charge of the functional groups and the metal speciation at different pH values are important aspects for the biosorption performance. At low pH values (in acidic conditions), metal ions are positively charged being attracted by the negatively charged biomass. With an increase in pH, the amount of hydroxyl ions is increased in the solution. Metal ions react with OH^- ions and precipitate at higher pH values, depending upon the solubility product constant (K_{sp}) values of the metal hydroxides. In general, metal ions are precipitated in the alkaline pH range making impossible the biosorption process. So, the upper limit of a metal solution pH must be studied.[6, 26] For example, the pH increase of Cr(VI) solution from 1 to 4 improves the negative charge on the dead *S. cerevisiae* biomass surface due to the deprotonation of the metal binding sites, hence attracting Cr(III) ions resulted from the reduction of Cr(VI), as indicated in the work of Hlihor *et al.*[52] The effectiveness of the reduction of Cr(VI) to Cr(III) increased with the decrease of pH from 4 to 1, while the total Cr concentration diminished with increasing the pH from 1 to 4.[52]



a)



b)

Fig. 1 – Biosorbent type influence on Cd(II) uptake (a) and on process efficiency R (%) (b) (50 mg/L Cd(II), 5 g/L biosorbent dosage, pH 6, PSH-Pumpkin seed hulls, BH-Bean hulls, S- straws, NS-nutshells).

Effect of temperature on biosorption efficiency – Thermodynamics

Temperature is found to be an important parameter for the sorption of metal ions dealing with the thermodynamics of the biosorption process and is directly related to the kinetic energy of the metal ions. Thus, it can account for the diffusion process. An increase or decrease in temperature should cause a change in the amount of metal sorbed by the biomass.[72]

According to Hlihor *et al.*[11] wastewater containing *Saccharomyces cerevisiae* biomass from certain segments of bakery industry could be redirected in the view of wastewater treatment in cadmium electroplating sectors. In this context, a maximum uptake of about 35 mg of cadmium per g of dried yeast and 86 % removal of metal solution was observed at 100 mg L^{-1} cadmium solution and 40 ^{o}C, with an equilibrium time of 24 hours.

The thermodynamic parameters in any biosorption process are calculated based on Eqs. (1, 2):[73]

$$\Delta G^0 = -RT \ln K_d \quad (1)$$

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^0}{RT} \quad (2)$$

where ΔG^0, ΔH^0, ΔS^0 and T are the Gibbs free energy, enthalpy, entropy, and temperature in Kelvin, respectively, K_d is the distribution coefficient and R is the gas constant. The values of enthalpy (ΔH^0) and entropy (ΔS^0) are obtained from the slope and intercept of of $\ln K_d$ vs. $1/T$ plots.

The distribution coefficient (K_d) is calculated from the concentration of heavy metal in suspension (C_i) and that of heavy metal in supernatant (C_e) after phases separation according to Eq. (3):

$$K_d = \frac{C_i - C_e}{C_e}\frac{V}{m} \quad (3)$$

where V is the volume of the solution (L) and m is the mass of dead biomass (g).

MODELING AND SIMULATION TOOLS FOR BIOSORPTION OF HEAVY METALS

The equilibrium data of heavy metal biosorption are represented by different modeling approaches. Different adsorption equilibrium and kinetic models are extensively used in elucidating the biosorption of heavy metals, indicating the need to highlight and summarize their essential issues.[17, 74]

Isotherms modeling

Biosorption equilibrium is the basic requirement for designing a biosorption system. Linear regression is frequently used for the determination of the best-fitting sorption isotherm, while the method of least squares is applied for finding the parameters of the isotherms. Since the transfer of substances from a mobile phase (liquid or gaseous) to a solid phase is a universal phenomenon, the "isotherm" – a curve describing the retention of a substance on a solid at various concentrations, is a major tool to describe and predict the mobility of metal ions in aqueous solutions. These retention/release phenomena are sometimes strongly kinetically controlled, so that time-dependence of the sorption isotherm must be specified.[75]

The adsorption equilibrium determines:[76]

1. the amount of species adsorbed under a given set of conditions (concentration and temperature), or
2. how selective retention takes place when two or more absorbable components co-exist. The equilibrium distribution of metal ions between the biosorbent and the solution is important in determining the maximum biosorption capacity.

Several isotherm models are available in the literature to describe the equilibrium biosorption distribution and the probable mechanism of the sorption process. Some of the most applied isotherm models in biosorption studies, Langmuir isotherm and Freundlich model, are summarized as the best fitting isotherms, in Table 4.

The linear representations of Langmuir model applied for the removal of Cd(II) ions onto mustard biomass and alkaline treated mustard biomass is presented in the work of Bulgariu *et al.*[37] The authors indicated that the value of correlation coefficient (R^2) was higher in the case of Langmuir model than for Freundlich model, meaning that both untreated and alkaline treated mustard biomass surfaces are up of homogeneous sorption patches, demonstrating the formation of monolayer coverage of Cd(II) ions on the outersurface of the biosorbent.

Table 4

Best-fitting isotherm models applied in the biosorption of heavy metals from wastewaters

Isotherm	Linear form	Biosorbents	References
Langmuir model	$\frac{C_e}{q_e}=\frac{1}{q_m}C_e+\frac{1}{K_L q_m}$ (4)	*Bacillus* sp. FM1/Cr(VI)/Cu(II)	51
		Olive tree pruning/Pb(II)	47
		Ulva lactuca sp./Pb(II)/ Cd(II)	77
		Deseeded sunflower head waste–based biosorbent/Cr(VI)	78
		Arthrobacter sp./As(III)/As(V)	79
Freundlich model	$\log q=\log k_F+\frac{1}{n}\log C_e$ (5)	*Ulva fasciata*, *Sargassum* sp./Cd(II)	80
		Bacillus sp. FM1/Cr(VI)/Cu(II)	51

where: K_L (L/g) is a constant related to the adsorption/desorption energy, q_m (mg/g) is the maximum sorption upon complete saturation of the biomass surface.
k_F ($mg^{1-n}g^{-1}L^n$) represents the sorption capacity when metal ion equilibrium concentration is equal to 1, and n represents the degree of dependence of sorption with equilibrium concentration.

Table 5

Best-fitting kinetic models applied in the biosorption of heavy metals from wastewaters

Kinetic	Linear form	Biosorbents/Metals	References
Lagergren pseudo-first order model	$\log(q_e-q_t)=\log q_e-\frac{k_1}{2.303}t$ (6)	*Sargassum* sp., *Turbinaria conoides*, *Ulva* sp./Hg(II)	30
Pseudo-second order model (Ho model)	$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{1}{q_e}t$ (7)	*Rhodococcus* sp. WB-12/As(III)	49
		Enteromorpha prolifera/Pb(II)	83
		Agaricus bisporus/Cd(II)/Zn(II)	60
		waste eggshell/Cu(II)	84
		Ficus hispida L./Pb(II)	85

where: q_e and q_t (mg/g) are the sorption capacity at equilibrium and at time t (min), respectively and k_1 is the rate constant of the pseudo-first order equation (min^{-1}).
k_2 is the rate constant of pseudo-second order sorption (g/mg min).

Kinetic modeling

Predicting the rate at which biosorption occurs for a given system is another important factor in biosorption system design, since adsorbate residence time and the reactor dimensions should be in accordance with the systems kinetics.[81] In spite of the importance of biosorption equilibrium studies, that determine the efficiency of the process, kinetic models were used to elucidate the mechanism of biosorption together with its rate-controlling steps. Furthermore, data on the kinetics of heavy metal uptake are necessary to select the best conditions for full-scale biosorption process.[82] In order to investigate the mechanism of biosorption, various kinetic models have been suggested. As shown in recent literature, the pseudo-second order model developed by Ho[81] describes better the biosorption process comparative to other models (Table 5).

New approaches for biosorption modeling and optimization

The study of the biosorption process can be extended with simulations based on various simulation tools. Among these, artificial neural networks (ANN) could represent an alternative tool for complex process modeling when complete phenomenological and experimental data are not available. For the consideration of ANN as a modeling and simulation tool for biosorption studies, input/output data must be known. The ANN method can take simultaneously into account several experimental parameters that affect the biosorption process, thus significantly diminishing the working time and the number of experiments necessary to carry out a complete adsorption study.[86-87] Another optimization tool applied with success for wastewater treatment is represented by genetic algorithms (GAs), which have the capability to find a global optimum with no piece of information in the search area other than an objective function that assigns a value to any solution.[87-88]

Suditu *et al.*[87] successfully applied the artificial intelligence method based on neural network models and genetic optimization algorithms for the removal of cadmium, cobalt, nickel, mercury, and copper from wastewaters by peat from Poiana Stampei, Romania. In the study of Singha *et al.*[89] the ANN with a single hidden layer trained with Levenberg-Marquardt algorithm predicted the percentage removal of Cr(VI) ions from aqueous solution accurately. The maximum removal of Cr(VI) ions by eight different biosorbents considering different operating parameters was studied to optimize the conditions for the biosorption process. Kardam *et al.*[90] developed a two-layer ANN model to predict the removal efficiency of Cd(II) ions from aqueous solution using shelled *Moringa Oleifera* seed (SMOS) powder by combining back propagation (BP) with principle component analysis. The ANN technique was applied by Gamze Turan *et al.*,[91] for the prediction of adsorption efficiency for the removal of Zn(II) ions from leachate by hazelnut shell. A comparison between the model results and experimental data gave a high correlation coefficient and showed that the model is able to predict the removal of Zn(II) from leachate. The removal of total chromium from aqueous solution by *Bacillus* sp. was modeled by ANN technique based on 360 data sets obtained in a laboratory batch study by Masood *et al.*[92] Their researches showed that the ANN model had reasonable predictive performance (R^2 = 0.971) of chromium biosorption.

Response Surface Methodology (RSM), which is a combination of mathematical and statistical techniques used for developing, improving and optimizing processes, has been also emphasized in recent years in the field of biosorption of heavy metals.[93-95] An extensive review that describes the use of response surface methodology (RSM) and artificial neural networks (ANN) in biosorption modeling and optimization was developed by Witek-Krowiak *et al.*[96] The authors discuss the limitations and application of these techniques in biosorption modeling and optimization and showed that these methodologies are especially useful in modeling and optimization.

DESORPTION

Biosorption studies are usually followed by desorption studies with the aim of recovering the metal retained and for the possible reuse of the biomass in subsequent cycles. Desorption of loaded biomass enables the reuse of the biomass, and the recovery and/or containment of biosorbed materials. In this frame, it is desirable that the desorbing agent does not significantly damage or degrade the biomass. In some cases, desorption treatments may further improve sorption capacities, while in other cases there may be a loss of biomass ability to retain heavy metal ions.[97]

Ahluwalia and Goyal[48] used a by-product of the fermentation industry as waste biomass for the removal of Cr(VI) from the acidic effluent of a metal processing industry. In batch sorption, 100% Cr(VI) removal was achieved from aqueous solution in 30 min contact at pH 4.0–5.0. Insignificant change in metal removal was observed up to 10 cycles. In the study of Jayaraman and Arumugam,[98] the desorption of Cu(II) from *Aspergillus flavus* was successfully done by recovering up to 80% of the adsorbed Cu(II) using 0.1 N NaOH and 0.1 N HNO_3. Joshi and Sahu[99] showed that HNO_3 is a more efficient elutant than $CaCl_2$ and NaCl, with more than 90% elution for Pb(II), Cd(II), Ni(II) and Zn(II) from *Mucor rouxii* while deionized water exhibited negligible desorption capability. Ogata *et al.*[100] showed that Raw Wheat Bran can be used in repeated and effective adsorption-desorption of Cd(II) and Pb(II) cycles by using 0.01 mol/L HCl or 0.01 mol/L HNO_3 solutions. Treatment of Zn(II) loaded *Scenedesmus* sp. biomass with 0.1 M H_2SO_4 in the study of Sarwa and Verma,[101] showed almost 99% recovery of zinc. The results demonstrated that the same biomass can be used for minimum five cycles for Zn(II) adsorption and recovery with similar efficiency.

The desorption process should yield the metals in a concentrated form, restore the biosorbent close to the original state for effective reuse with undiminished metal uptake and no physical changes or damages to the biomass.[102]

BIOSORPTION MECHANISM

The distribution of different elements and compounds species in water is highly dependent on pH, composition, temperature, and the oxidation-reduction potential of the solution. These variables define their precipitation, dissolution, and complexation reactions. Especially for the metallic ions, phenomena such as chemical and biological transformations, metal mobility, bioavailability, bioaccumulation, toxicity, and persistence in the environment frequently depend on the chemical form or speciation of a given ion.[103] The mechanisms involved in metal bonding need to be well understood and the metal speciation in aqueous solutions has to be taken into consideration as it plays an important role.[104]

The microorganisms structure, which is quite complex, indicates several paths for heavy metal entrapment. Some of these mechanisms for metal species removal were described in detail by Kotrba[105] and include: extracellular immobilization, precipitation, intracellular detoxification, solubilization and mobilization of metals. Gaur *et al.*[106] also explained the main mechanisms involved in the biosorption of heavy metals (Fig. 2).

Several techniques are used for the elucidation of biomass-heavy metal interaction. Depending on the biosorbents nature the tools used in this purpose are: Fourier Transform Infra-Red (FTIR) spectroscopy, X-ray Photo Electron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Energy Dispersive X-ray (EDX) fluorescence spectroscopy, Brunauer-Emmett-Teller (BET) Surface Area Analysis etc.

These methods are commonly combined to obtain a complete description of the structure, morphology and composition of the biosorbents.[107] For example Diaconu *et al.*[108] concluded that, due to the nature of the cellular components, several functional groups are present on the microorganism cell wall, including carboxyl, phosphonate, amine and hydroxyl groups. As they are negatively charged and abundantly available, carboxyl groups actively participate in the binding of metal cations. The mechanism of metal biosorption varies according to the metal species and type of biosorbent. Scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX) and transmission electron microscopy (TEM) were used by Srivastava and Thakur[109] to assess morphological changes and confirm chromium biosorption by *Serratia* sp. The results indicated that a combined mechanism of ion-exchange, complexation, co-precipitation and immobilization was involved in the biosorption of chromium by bacterial cells. In the case of pretreated non-living biomass of *A. niger* used in the study of Amini *et al.*,[110] it seems that ionic, chemical and physical forces of adsorption were involved in metal uptake processes; a variety of ligands located on the cell wall of biomass were responsible in metal chelation. The FT-IR analysis proved that Ni(II) might be bound to oxygen atoms from functional groups of carbonyl (–C=O) and hydroxyl (–OH) on the cell surface of *A. niger* biomass. Zhang *et al.*[111] showed by potentiometric titration that ethanol and caustic pretreatment remarkably increased the quantity of carboxyl and amino groups of baker's yeast biomass. Zeta potential of the biomass changed both before and after biosorption. FT-IR data also indicated that functional groups on the surface of baker's yeast cell were changed by caustic and ethanol-pretreatment and that carboxyl, amino and hydroxyl groups were mainly involved in a chelation and coordination interaction during the biosorption of Cu^{2+} process. Arief *et al.*[107] have elaborated a complex review with specific details regarding the characteristics of biosorbents followed by the presentation of biosorption mechanisms for the removal of a variety of metals on diverse types of biosorbents. Considering diverse combinations of FT-IR, SEM-EDX, TEM as well as classical methods such as titration-extremely useful in determining the main processes on the surfaces of biosorbents, the researchers pointed out as the most prevalent mechanisms for the biosorption of most heavy metals are ion exchange and complexation. In addition, Arief *et al.*[107] consider that functional groups represented by carboxyl, hydroxyl, sulfate and amino groups play significant roles in the biosorption process.

Therefore, the physical and chemical characteristics of biosorbents analyzed using different available tools are important for understanding the metal binding mechanism on the biomass surface. When the metal-biomass interaction mechanisms are reasonably understood, this will open the possibility to simplify the screening process by selecting the most promising and low-cost biosorbents and for biosorption optimization on molecular level.[17, 20]

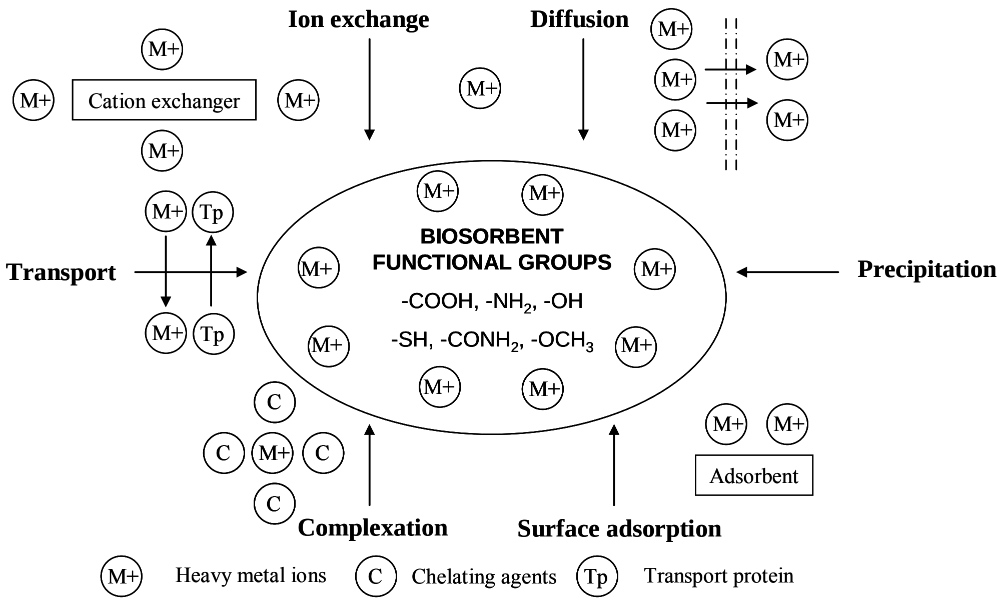


Fig. 2 – Biosorption mechanisms categorized based on cellular metabolism and location of biosorption (adapted after Gaur *et al.*[106] and Gavrilescu[17]).

CONCLUSIONS AND RECOMMENDATIONS

Future trends in biosorption will take into consideration the identification of better and more selective biosorbents, new directions for modeling and optimization of the process in order to a better understanding of the metal-biomass interactions, as well as for process scale-up. Taking into account the high variety of proposed biosorbents, further assessments on market size, costs of development and commercialization of biosorption as an optimum bioremediation technology are highly expected. A better understanding of metal-biomass interactions should open the possibility for mechanisms elucidation.

A frequently asked common question involves the fate of the metal loaded biomass after the biosorption process. The common answer to the disposal of the final material is via landfill or incineration. Even if the biosorbent can be efficiently reused over several cycles, the final disposal of the material should be addressed. However, due to the increasing levels of landfill tax, and the potential restrictions due to contamination of ground waters, the landfill option has become less attractive.

A variety of investigations clearly demonstrated that biosorption is a useful option to conventional treatment systems for the removal of heavy metals from aqueous solutions.

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