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Chapter 3

Biosorption of Multicomponent Solutions: A State of the Art of the Understudy Case

Filomena Costa and Teresa Tavares

Additional information is available at the end of the chapter

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Abstract

Although there has been an intense study and exploitation of research regarding biosorption processes, the lack of coherent and similar methodologies, essential to the elaboration of any consequential and universal conclusion, associated with the lack of biosorption studies conducted at a pilot and industrial scale, with multicomponent solutions or real effluents, as well as the lack of information regarding the pollutant interactions makes the implementation and commercialization of biosorption technology very complicated. This chapter summarizes the existing knowledge and the experimental work conducted at a pilot scale or industrial scale with multicomponent solutions and critically reviews aspects related to biosorption research regarding the advantages, the disadvantages, the rationale, the scope and scientific value of biosorption processes and the obstacles to commercial success.

Keywords: biosorption, bioremoval, metals, organic pollutants, pilot and industrial scale

1. Introduction

Although the contamination of water resources is a widely recognized fact and a critical universal issue, it is still a common occurrence [1, 2]. The major sources of aquatic as well as terrestrial and atmospheric systems contamination are effluent outfalls and gas emissions from industries, agricultural activities and refinery contaminants [2] that end up entering water bodies via rain water, soil and groundwater systems. The contaminants comprise (i) inorganic chemicals such as metals, extensively used in a wide variety of industries, including metal plating, mining, batteries, electroplating, ceramic, chemical manufacturing of paint and coating, health-care

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products, extractive metallurgy, petrochemical and fine chemistry [3] and (ii) organic chemicals such as industrial solvents, volatile organic compounds (VOCs), pharmaceuticals, insecticides, pesticides, dyes [1] and food processing wastes [2].

The non-natural redistribution of these chemicals has culminated first in their increasing discharge and accumulation into the different environmental matrices and second in the development of environmental and health problems (**Figure 1**) [3, 4]. Therefore, there is a constant search for economical, efficient, effective and eco-friendly processes able to not only decontaminate wastewaters but also ensure that the presence of the pollutants discharged into the aquatic systems is below the permissible limits.

In the past decades, great attention and concern have been given to the continuous and increasing discharge of metals such as chromium, mercury, lead [2], cadmium and nickel into the environment. This increasing concern is due to metals' inherent properties, (i) persistence in nature, (ii) tremendous toxicity even at low concentrations and (iii) tendency for bioaccumulation via food chain in living tissues, which may culminate in the triggering of several serious diseases and health disorders [3].

Chromium compounds, for instance, are carcinogenic and nephrotoxic in nature. Exposure to mercury and lead may provoke allergic skin reaction, eventual negative reproductive effects as well as damage to brain function and disruption of the nervous system [2]. Cadmium exposure may cause severe damage in different organs including the testis, lungs, liver and kidneys and even lead to infertility [5, 6]. It also affects the action of enzymes and induces genomic instability through complex and multifactorial mechanisms, such as proteinuria, and an increase in the frequency of kidney stone formation, eventually causing certain types of cancer (group B1) [3]. Besides being listed in the carcinogenic group B2, nickel has been implicated as a teratogen nephrotoxin and an embryotoxin element. Acute and chronic nickel exposure can cause several disorders such as cyanosis, chest pain, tightness, pulmonary fibrosis, skin dermatitis, lungs and kidney damage and renal oedema [7].

The capacities of metals to disrupt the function of fundamental biological molecules, such as DNA, proteins and enzymes, and to displace certain metals essential for the cell viability by

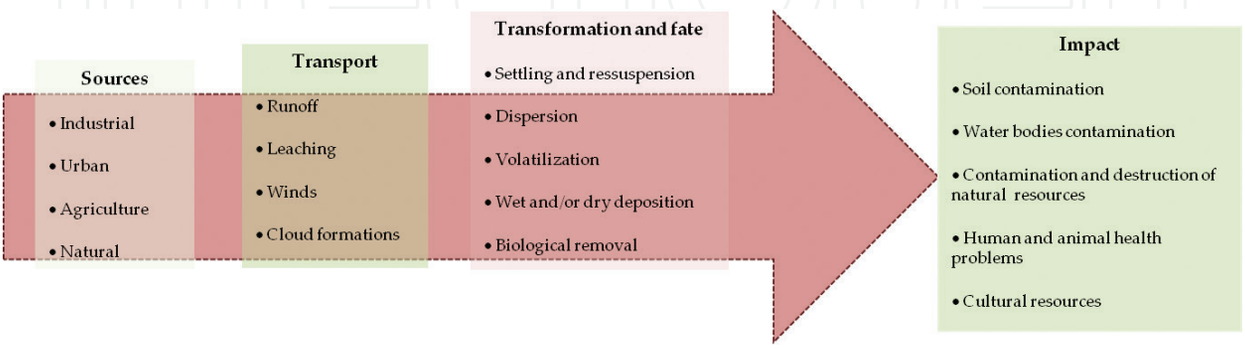


Figure 1. Sources of pollution by organic and inorganic chemicals, their transport, transformation, fate and impact into the different environmental matrices.

similar metals are the two major causes of their toxicity. For instance, lead can replace calcium in the bone and other tissues where it is required, whereas cadmium can replace zinc in some proteins that require it for their structure as well as function [2].

More recently, the discharge of organic chemicals such as pharmaceutical products [8], volatile organic compounds, aromatic hydrocarbons [9] and dyes [10] has also caught the world attention, due not only to their persistence, toxicity and mobility in the environment but also to their widespread use and discharge as well as their impact on all forms of life.

Despite the fact that every single aspect connected to pharmaceutical efficiency and patient security to be under scrutiny [8], the complete extent and consequences of the presence of emerging pollutants in the environment matrices and on the wellbeing of all forms of life are not yet sufficiently studied in terms of toxicity, degradability and occurrence, allowing it to remain unregulated.

Pharmaceutical compounds have been detected at trace concentrations (ng/L levels) in a wide variety of environmental water samples including sewage flows, rivers, lakes, groundwater aquifers and drinking water [11]. Although the concentrations of these pharmaceutical products have been detected at trace concentrations in a broad variety of aquatic environments, their continuous input may compose a potential threat for living organisms. Furthermore, pharmaceutical products are often synthesized in order to remain unchanged during their passage through the human body, which makes them and their metabolites persistent pollutants in environmental matrices [8].

The increased use of organic compounds in almost, if not all, industrial sectors as well as in household activities and consequent discharge and accumulation into the environment has increased in an extremely significant way in the past years [2, 12–14]. Most of these compounds are extremely toxic to humans due to (i) their general carcinogenic and mutagenic properties, (ii) their capacity to form intermediates with the same or even the higher level of toxicity [15] and (iii) their persistence and mobility into the different environmental matrices [7].

More than 1×10^5 dyes are currently marketed with an annual production exceeding 7×10^5 tons per year, of which about 2% are discharged directly to effluents from manufacturing operations, whereas 10% are discharged from textile and related industries [16]. The dye lost through the practices of textile industry poses a serious problem for wastewater management and treatment, since it can reach loss values as high as 50%. About 2×10^5 tons of dyes are discharged annually into the environment, especially into water bodies [17].

Although chemical precipitation, reverse osmosis, complexation, solvent extraction, ion exchange, adsorption on granular activated carbon, condensation, thermal degradation, oxidation and incineration comprise the conventional abiotic methods usually employed to remove different types of pollutants from effluents [7], biotic methods such as water purification treatments and standard sewage as well as auxiliary reed bed and wetlands approaches [18] have been used for many years. The outstanding ability of microorganisms to detoxify organic and inorganic pollutants [15, 18] and to the downside of the abiotic methods which can be summarized (i) as expensive, (ii) not environmentally friendly and (iii) usually dependent on the concentration of the waste [7] makes them an attractive alternative to decontaminate contaminated solutions.

2. Biosorption: a general overview

Microorganisms, in particular bacteria and fungi, have been receiving particular attention in the area of environmental microbiology and biotechnology due to their ability not only to decompose a wide range of organic compounds, from natural and anthropogenic origin, but also to accomplish changes in the speciation and mobility of metals and radionuclides as well as other inorganic elements by oxidation-reduction and other changes, most of which are a direct consequence of metabolic properties of living organisms and microorganism [18].

Although the term *biosorption* presents a multidimensional character, its definition is rather difficult and has been evolving over the past few decades, due to the diversity of the mechanisms that contribute to the overall process, depending on the sorbate and the biosorbent, on the environmental conditions and on the metabolic processes in the case of living organisms [18, 19].

Some publications [18, 20, 21] indicate that most researchers define biosorption as a passive and metabolically independent process that can be performed either by dead biomass or fragments of cells and tissues or by living cells as an active and metabolic-dependent process. It is important to highlight that both mechanisms can overlap adding additional confusion in the use of the terminology.

It is also important to highlight that (i) biosorption is a crucial part of many processes taking place in nature, including, for example, antigen-antibody immune reactions and adsorption to host cells, as the first stage in virus replication or sorption in soil and that (ii) numerous methodological approaches used in medicine, life sciences and biotechnology are, in fact, based on biosorption processes, for instance, the staining of microbial cells for electron microscopy and targeted therapies in cancer treatment. It is therefore possible to affirm that many life phenomena are in some way related to interactions between a sorbate and biological surfaces [18]. Basically, biosorption is a reversible and rapid process of binding of ions or neutral molecules from aqueous solutions onto functional groups that are present on the surface of biomass, independent on cellular metabolism, efficient and selective [21].

Presently, it is accepted that biosorption is a physico-chemical process, simply defined as the removal of substances from solution by biological material, and includes mechanisms such as absorption, adsorption, surface complexation ion exchange and precipitation [18]. The addition of the prefix *bio* to the term *sorption* denotes the involvement of a biological entity (living or death biomass, as well as their metabolites or synthesized products). Although the majority of biosorption research has been focused on metals and/or metalloid species, the substances to be sorbed can be from either organic or inorganic origin and presented in soluble or insoluble forms. Therefore, considering the diversity of sorbates and sorbents that can be used in all domains of life, it is plausible to use the term biosorption to describe any system where a sorbate (e.g. an atom, molecule, a molecular ion) interacts with a biosorbent (a solid surface of a biological matrix) resulting in an accumulation at the sorbate-biosorbent interface and therefore a reduction in the solution sorbate concentration.

The mesmerizing features of biosorption processes over traditional treatment methods comprise (i) economical operating costs; (ii) inexpensive biological materials, usually obtained from

agriculture or from industrial wastes; (iii) high efficiency; (iv) no additional nutrient requirement; (v) minimization of biological or chemical sludge; (vi) biosorbent regeneration; and (vii) the possibility of metal recovery. In addition to all this captivating features, biosorption processes can be accomplished in an extensive range of pH values (from pH 3 to pH 9) and temperature values ranging from 4 to 90°C.

The first paper on biosorption was published in 1951, and since then, enormous efforts have been made to accomplish efficient, effective and economic biosorbents to be employed in wastewater treatment. Fundamental progresses have been accomplished over the past decades in order to understand the complex biosorption mechanisms, the methods for its quantification (equilibrium and kinetics) and the factors that influence efficiency and the rate of the process (**Figure 2**) [20].

Although the majority of the biosorption research conducted till now has been performed on microbial systems, mainly bacteria, microalgae and/or fungi, with metals and related substances (**Table 1**), the term is now being applied to all types of organic compounds and to particulates.

The massive research concerning biosorption of metals is an unsurprising fact, taking into account not only the toxicity effect and increased discharge of these contaminants into the environment but also the nature of adsorption and ion exchange mechanisms. Nevertheless, it is also crucial to highlight that regardless the continuous increase in published research related to the biosorption of hazardous substances and/or elements, there has been little or no exploitation in a pilot and industrial scale and/or context [18] and on the decontamination of multicomponent solutions [3, 4, 7, 22, 23]. In fact, despite the biosorption process that has been discussed in literature for 60 years with over 13,000 scientific papers in peer-reviewed journals [19], so far most of this research was performed in a laboratory scale, using batch tank reactors or packed mini-column, and has not been extensively implemented in an industrial scale and in multicomponent solutions. The team of Professor Bohumil Volesky from McGill University, Canada, and his company BV Sorbex comprise the few researchers that have contributed to

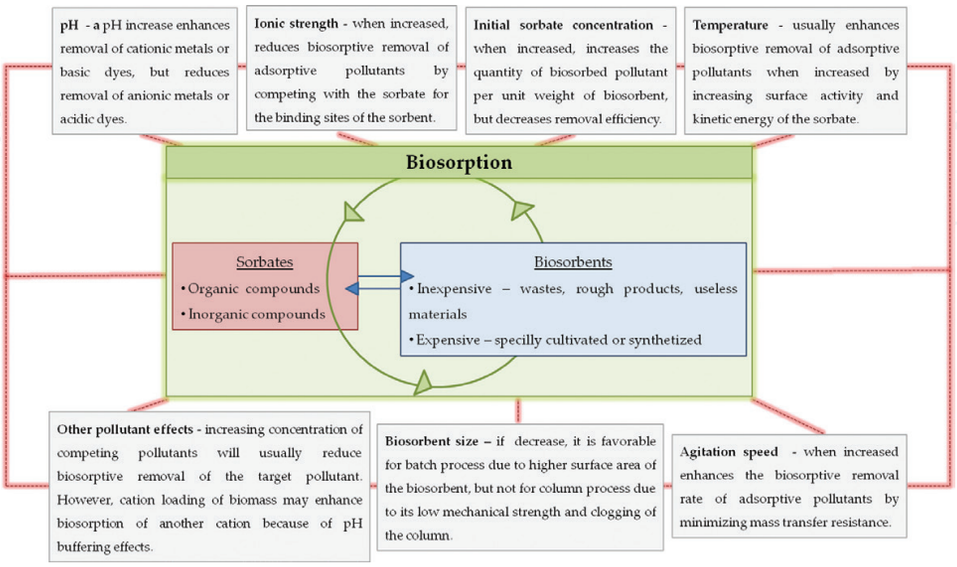


Figure 2. Biosorption process: a global overview (adapted from Refs. [2, 19]).

Position	Paper	Times cited
1	Review of second-order models for adsorption systems *Journal of Hazardous Materials* 136 (3): 681–689	1402
2	Biosorption of heavy metals *Biotechnology Progress* 11 (3): 235–250	1323
3	A review of the biochemistry of heavy metal biosorption by brown algae *Water Research* 37 (18): 4311–4330	1133
4	Application of biosorption for the removal of organic pollutants: A review *Process Biochemistry* 40 (3–4): 997–1026	1002
5	Biosorbents for heavy metals removal and their future *Biotechnology Advances* 27 (2): 195–226	903
6	Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature *Progress in Polymer Science* 33 (4): 399–447	832
7	Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste *Dyes and Pigments* 54 (1): 47–58	759
8	Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water *Journal of Hazardous Materials* 137 (2): 762–811	757
9	Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies *Environmental Science & Technology* 36 (9): 2067–2073	749
10	Interactions of fungi with toxic metals *New Phytologist* 124 (1): 25–60	740

Table 1. The top 10 publications in the ISI Web of Science database (Web of Science Core Collection) for 'all years' (1970–2016) with 'biosorption' in the topic.

the scale-up of sorption process field, from a laboratory scale to a pilot or industrial scale [21]. The team of the Centre of Biological Engineering from the University of Minho, Portugal, has also been contributing to the study and understanding of (i) the scale-up of biosorption processes from a laboratory scale to a pilot scale and (ii) the increase of solution complexity to be decontaminated, evolving from single-component solutions to multicomponent solutions, mixing organic and inorganic compounds [3, 4, 7, 9, 15, 24], the main subject of this chapter.

3. Biosorption in multicomponent solutions

Although most of industrial and household effluents and wastewater are composed by a cocktail of contaminants made of metal residues and organic compounds, few studies regarding the simultaneous removal of multicomponent solutions have been conducted and optimized, studies that would better simulate the behaviour of the pollutants present in real effluents. The effect that different types of contaminants (inorganic versus inorganic and inorganic versus organic) have on each other and the effect that different initial concentrations of metal exert on the bioremoval (biodegradation and biosorption among other biological processes)

of the organic contaminant have also been poorly investigated. For these reasons, the authors opted to review the state of the art of biosorption from multicomponent solutions, from a laboratory scale to a pilot and/or industrial scale.

Costa and Tavares [3] studied the ability of two fungi and one bacteria (*Penicillium* sp., *Alternaria* sp. and *Streptococcus equisimilis*) to simultaneously treat tertiary solutions containing diethylketone, Cd(II) and Ni(II), and they determined the influence of the initial concentration of metal on (a) the microbial growth, (b) the biosorption capacity of these pollutants and (c) the biological activity after exposure. The results obtained regarding the tertiary solutions allowed to infer that *S. equisimilis* presented the best performance in terms of uptake, for all the conditions tested and that an increase in the initial concentration of metal promoted an increase in the uptake. For the same experimental conditions, the biosorption data obtained for the three microorganisms showed (i) a higher affinity of the biosorbents towards Ni(II) and (ii) a strong and detrimental effect of the metals either in the biosorption process or in the microbial growth. These results may be explained by the fact that not only Ni(II) can be used by the cells as a cofactor, competing actively and passively with Cd(III) but is also less toxic than Cd(II).

More complex systems were further evaluated [4] with a suspended bacterial culture of *Streptococcus equisimilis* with different initial concentrations of Ni(II) (5–450 mg/L) and Cd(II) (5–100 mg/L) in single-component solutions compared to vermiculite to decontaminate single-component solutions composed either by diethylketone, Cd(II) or Ni(II) and binary-component solutions composed either by diethylketone and Cd(II) or diethylketone and Ni(II). A *S. equisimilis* biofilm supported on vermiculite to decontaminate binary solutions composed either by diethylketone and Cd(II) or diethylketone and Ni(II) was also evaluated. The principal aim of this research was the characterization of the interactions between the different concentrations of sorbates and the biosorbents used, when employed in single or binary solutions. For the first set of experiments (*S. equisimilis* and different concentrations of Ni(II) or Cd(II), it was observed that the uptake and percentage of influent Ni(II) sorbed depended on the initial concentration of the sorbate. No significant pH changes had occurred, and the uptake suffered a 30-fold increase with the increase of the initial concentration between 5 and 80 mg/L. Nevertheless, there were no significant changes (<10%) in terms of biosorption percentage for the same initial concentration. The biosorption of Cd(II) was also found to depend on the initial concentration, suffering fluctuations lower than 18%. In these assays, there was an increase in terms of pH (from 6.05 to 6.98). This increase resulted in an increase in the hydroxyl and other anionic functional groups, which made the bacterial surface more negative increasing the number of electrostatic interactions. For the second set of experiments, it was observed that the presence of Cd(II) decreases significantly the sorption percentage of diethylketone, but the presence of this organic compound increased Cd(II) sorption percentage. The presence of Ni(II) has a synergetic effect on diethylketone biosorption. For the third set of experiments, it was established that the presence of the biofilm is an advantage, obtaining promising results, specially taking into account not only the concentrations employed but also the toxicity of the metals. In these experiments, a common increase in terms of sorption efficiency was observed, and this may be explained by the functional groups present on the biofilm that can implement the substrate molecule adsorption and eventually promote the biodegradation of diethylketone and by the increase of the available sites for sorption.

Attempting to mimetize the complexity of real effluents and wastewaters, biosorption experiments of multicomponent solutions (Al(III), Ni(II), Cd (II) and Mn(II)) by a *S. equisimilis* biofilm supported into vermiculite were performed first at a laboratory scale in batch system (4 g/L of diethylketone and 5–100 mg/L of each metal) and second at a pilot scale in open systems (7.5 g/L of diethylketone and 100 mg/L of each metal) [7]. Diethylketone was periodically added to the bioreactor and was used as the only carbon source. At laboratory scale, the authors observed that diethylketone and removal percentages higher than 95% were achieved in less than 4 hours for all the initial concentrations of metal tested and that the increase of the initial concentration of metals accelerates the complete bioremoval (by biodegradation and/or biosorption processes, for instance) of diethylketone. Regarding the results obtained for the four metals (5–80 mg/L), it is was found that they follow the sequence Al(III) > Cd(II) ≥ Ni(II) ≥ Mn(II), whereas for the experiment conducted with an initial concentration of 100 mg/L, the bioremoval efficiency followed a different sequence Al(III) > Ni(II) > Cd(II) > Mn(II). This difference may be explained by the increase in the initial concentration of metal, which will influence the ionic strength of the elements in solutions, and also by the fact that many divalent metal cations are structurally similar, allowing the substitution of essential metals, such as Ni(II) and Mn(II) for non-essential metals such as Cd(II). The uptake of all metals increased with the increase of the initial concentration of each metal.

At a pilot scale, it was observed that the biosorption percentage of all the sorbates (organic and inorganic) tended to increase through time and followed the sequence diethylketone > Al(III) > Cd(II) ≈ Ni(II) ≥ Mn(II), and this is explained by the bioavailability and structural similarity between Ni(II) and Cd(II) that promote the uptake of Cd(II) by the cell enzymes instead of Ni(II) and by the combination of the reduced size of the ionic radius of Mn(II) associated with its reduced electronegativity and the small porosity of the support. The complete bioremoval of diethylketone and its metabolites was achieved, even after the addition of diethylketone to the bioreactor and the sorption percentage of each metal increased through time.

The effect of different initial concentrations of Cd(II), Cu(II), Zn(II), Pb(II) and As(II) (10 mg/L or 100 mg/L) on the bioremoval of fluorene (10 mg/L) by *Sphingobacterium* sp. KM-02 was also assessed [25]. The presence of those metals at 10 mg/L decreased fluorine bioremoval, and the microbial growth and the inhibition effect followed the trend Cd(II) ≈ Cu(II) > Zn(II) > Pb (II) > As(II). Cd(II) and Cu(II) strongly inhibited fluorene bioremoval and microbial growth, whereas Zn(II) and Pb(II) exert a modest inhibitory effect. As(II), on the other hand, has no negative effect on microbial growth and fluorene bioremoval.

3.1. Correlation between metal concentration and microbiological processes

Metals including cadmium, chromium (III and VI), copper, lead, mercury, nickel and zinc are reported to inhibit microbiological processes such as acidogenesis, methanogenesis, nitrogen transformation, biomass production and enzymatic activity [22]. *S. equisimilis* exposure (in the form of biofilm supported into vermiculite or in suspension) to solutions containing either Cd(II) or Ni(II) (5–100 mg/L) led to microbial growth inhibition [3, 4]. Nevertheless, it is important to mention that the addition of metals may also have the opposite effect and enhance and/or stimulate microbiological processes. The growth of a suspend culture

of *Alternaria* sp. and *Penicillium* sp. when exposed to Ni(II) concentration ranging from 5 to 100 mg/L was enhanced [3], and when this metal was mixed with diethylketone, the entrapment metabolic pathway selected by those microorganisms was different, since no metabolite was formed during the experimental period, as opposite to what occurred when exposed only to diethylketone.

Although studies concerning the influence of metals on organic contaminant bioremoval are scarce, it has been demonstrated that those elements are able to inhibit organic contaminant bioremoval, under both aerobic and anaerobic conditions.

Cadmium, chromium (II), copper, mercury and zinc were found to inhibit the biodegradation of 2,4-DME in lake water samples inoculated with either a sediment or an aufwuch (floating algal mat) sample [26]. In the aufwuch samples, mercury revealed to be the most toxic metal, with a microbial inhibitory concentration (MIC) of 2×10^{-3} mg total mercury/L, whereas in the sediment samples, zinc was the most toxic metal with a MIC of 6×10^{-3} mg total zinc/L. Naphthalene (NAPH)-degrading *Burkholderia* sp. was used in a pure culture and reported a MIC of 1 mg solution-phase cadmium/ L [27]. Comparable values of MIC were reported for cadmium (0.629 mg total cadmium/L for aufwuch samples and 0.1 mg total cadmium/L for sediment samples) [26].

Not all studies were focused on the effect of single metals on bioremoval of a single, pure organic pollutant. Benka-Coker and Ekundayo [28] investigated the impact of copper, manganese, lead and zinc on crude oil biodegradation by *Pseudomonas* sp. and *Micrococcus* sp. These authors inferred that the crude oil was mostly reduced by zinc and slightly by manganese. Interestingly, combinations of these metals presented a lesser toxic profile than some single metals. For instance, toxicity of 0.5 mg total zinc/L was mitigated by the addition of 0.5 mg total copper, lead and manganese/L.

3.2. Correlation between metal concentration and bioremoval inhibition

It is acknowledged that the bioremoval of an organic pollutant decreases as the concentration of bioavailable metal increases in co-contaminated systems (**Figure 3**). However, this pattern is not always observed. Two other additional patterns describing the effect of metals on the bioremoval of organic pollutants have been shown.

Low metal concentration enhances bioremoval of organic pollutant; high metal concentrations inhibit it—additional pattern 1: diverse studies showed a pattern of metal toxicity in which low metal concentrations enhance bioremoval activity, till the maximum level of stimulation is reached. After this point, an increase in metal concentration will lead to an increase in metal toxicity (**Figure 3**, Line 2). Sustaining this pattern is the result obtained by Capone et al. [29] showing that methanogenesis was enhanced by the addition of some metals.

Bioremoval inhibition of organic pollutants is due to low metal concentration; lower bioremoval inhibition of organic pollutants is due to high metal concentration—additional pattern 2: several studies suggested that low concentrations of metal strongly inhibit bioremoval activity, until a maximum of inhibition is achieved (**Figure 3**, Line 3). After this point, an

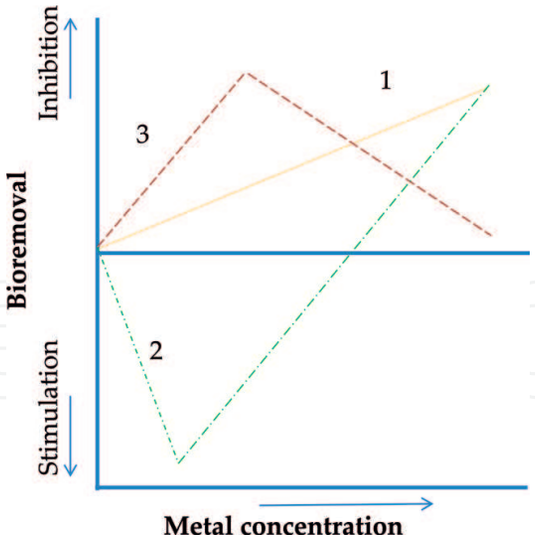


Figure 3. Metal concentration impact on bioremoval inhibition pattern of organic pollutants, assuming (1) a direct or linear relationship, (2) additional pattern 1 and (3) additional pattern 2.

increase in metal concentration will lead to a decrease of metal toxicity. An example is the work conducted by Said and Lewis [26] where an increase in metal concentration was responsible for a decrease in 2,4-DME bioremoval.

Briefly, the existence of different patterns of responses of organic pollutants towards metals is possible to assume and that this variety of responses makes the understanding and prediction of metal toxicity in the environment more difficult, since these elements may influence both the ecology and physiology of the pollutant-degrading microorganisms.

Unless the models used to predict the influence of metals on the bioremoval of organic pollutants incorporate both the ecologic and physiologic effects of metals towards the pollutant-degrading microorganisms, they may fail their main purpose.

3.3. Biosorption in multi-metal solutions

As previously mentioned, despite the research concerning biosorption processes has been well documented in the literature, biosorption of different metal ions by different types of biological materials has been mainly conducted in single-metal solutions [21]. Information concerning biosorption studies in binary- [30–34], tertiary- [31–35] and quaternary-component solutions [36] is very scarce. Moreover, the use of different evaluation methodologies makes any attempt to draw any meaningful and universal conclusion very difficult and, on the other hand [37], the influence that anions may exert on the biosorption process of metal cations has been somehow neglected.

Nostoc muscorum, a cyanobacterium indigenous from coal mining sites, was employed as biosorbent to decontaminate aqueous solutions containing Cd(II), Cu(II), Pb(II) and Zn(II) (5 or 10 mg/L) [38]. The results obtained in these experiments showed a maximum bioremoval of both Pb(II) (96.3%) and Cu(II) (96.4%) followed by Cd(II) (80.0%) and Zn(II) (71.3%) after 60 h of culture period. The bioremoval of Cd(II), Cu(II) and Pb(II) was maximum at 5 mg/L, whereas Zn(II) bioremoval has a maximum when all the four heavy metals were set at 5 mg/L. These

results suggest a dependence of metal bioremoval by *N. muscorum* on the metals and their concentration combination in the multi-metal solution. It was also observable that the metals' uptake depended upon their concentration combination in solution and the bioremoval order observed was Pb(II) > Cu(II) > Cd(II) > Zn(II). In this study, Pb(II) showed not only a better bioremoval efficiency compared with the other three metals but also that its bioremoval was unaffected by the presence of the three other metals. However, the presence of Pb(II) exerted a strong negative effect on the bioremoval of all other metals. These results may be explained by taking into consideration the Pb(II) strong interaction with the functional groups present on the biomass and because Pb(II) presents the smallest radius among the four metals tested in these assays (the smaller the hydrated radius, the higher is the affinity of its binding).

3.3.1. Effect of anions

Three aspects related to the influence of anions on the biosorption processes are usually considered in the available literature: (i) the influence that the anion has on the maximum biosorption capacity of the sorbent, in single-metal solutions [39]; (ii) the influence of anion concentration on the biosorption of several metal ions, in multi-metal solutions [37–41]; and (iii) the nature of the biosorbent that can influence significantly the effect of the anion on the biosorption capacity [21].

The biosorption of four metals—Cr(VI), Co(II), Ni(II) and Zn(II)—by the *Aspergillus niger* fungus [40] revealed that the presence of anions such as NO_3^- and SO_4^{2-} did not significantly affect the biosorption performance of the four metals, whereas the presence of Cl^- did negatively affect the biosorption performance of the four metals in multi-metal solutions.

Kuyuca and Volesky [42] studied the biosorption of Co(II) ions in the presence of SO_4^{2-} and PO_4^{3-} by the brown macroalga *Ascophyllum nodosum* and concluded that the presence of these anions did not reveal any influence on the biosorption performance, as opposite to the presence of NO_3^- anions, that strongly inhibited the biosorption process. The opposite situation was observed in the biosorption of Zn(II) by the cyanobacterium *Oscillatoria angustissima* [41], and it was stated that the presence of SO_4^{2-}, NO_3^- and Cl^- had the following biosorption inhibition order $SO_4^{2-} > Cl^- > NO_3^-$.

The degree of inhibition for the biosorption of La(III), Cd(II), Pb(II) and Ag(I) cations, by the *Rhizopus arrhizus* fungus [43], usually followed the order EDTA > SO_4^{2-} > Cl^- > PO_4^{3-} > glutamate > CO_3^{2-}.

As referred previously, the influence of the anion on the biosorption capacity will vary depending on the metal ion oxidation state, as it was observed for the biosorption of Cr(III) and CR(VI) ions [44], with the following inhibitory orders $SO_4^{2-} > Cl^- \approx NO_3^-$ and $NO_3^- > SO_4^{2-}$.

3.3.2. Effect of the ionic concentration

Considering the limited number of active sites present on the biosorbent surface, it is accepted that the biosorption capacity of the biosorbent towards a specific pollutant (metal or not) in a multicomponent solution is inferior to the one in single-component solutions; therefore, the contaminants will compete for the active sites, available for sorption [44].

This is the case of the amount of Cr(VI) biosorbed per unit weight of *Rhizopus arrhizus* that decreased with the increase of Fe(III) concentration as an antagonistic effect [45, 46].

Fagundes-Klen et al. [47] observed that the amount of Zn(II) biosorbed by *S. filipendula* in the presence of high concentrations of Cd(II) decreased significantly (56.8 %) when comparing the biosorption results achieved in single-metal solution. These results are easily explained by the reduced number of coordination, the ionic radius and the higher ionization potential of Zn(II).

It is therefore worth noting that as the ionic concentrations become higher, there is a growing force able to overcome the mass resistance transfer of metal ions through the biosorption process. The published data [48] showed that even though lead ions (Pb^{2+}) have higher affinity than copper (Cu^{2+}) to be biosorbed by an algae belonging to the genera *Gelidium* uptake, Cu^{2+} uptake was higher than Pb^{2+} uptakes due to the higher initial concentration of Cu^{2+}. Similar results described the biosorption of Pb^{2+} and Cu^{2+} by pine cone shells [49]. When binary solutions were tested, the uptake of both metals was significantly inhibited, revealing an antagonistic effect.

3.3.3. Effect of electronegativity and atomic weigh of metals

In multi-metal solution, the electronegativity and atomic weight of metals can also have an important role in the biosorption process and efficiency. Biosorption experiments showed that when mixed, Ni(II) and Zn(II) sorption by wheat straw presented different performances, revealing a competition between both metals for the actives sites present on the biosorbent surface and a higher preference for Zn(II) rather than Ni(II) [50]. These results are easily justified taking into consideration the more appealing physical characteristics of Zn(II): lower electronegativity and higher atomic weight of Zn(II). The oxygen-containing group present on the wheat straw (negative sites) repels Ni(II) more than Zn(II), making it more difficult to be sorbed.

3.3.4. Effect of temperature

As previously mentioned (see Section 2, **Figure 2**), temperature also plays an important role on the biosorption processes, as well as on all biological and physico-chemical processes. The biosorption of Cr(III), Cu(II) and Zn(II) by wine-processing waste sludge (WPWS) in a ternary system was found to be significantly affected by temperature. At normal conditions, the biosorption of these three metals in a mixture by WPWS followed the trend Cr(III) > Cu(II) > Zn(II). However, when the temperature decreases to 10°C, the biosorption of Cr(III) was inferior than Cu(II) [50].

4. Critical assessment concerning the biosorption research on multicomponent solutions

As previously mentioned, in the past few decades, there has been an intense study and research concerning biosorption processes to treat contaminated environmental matrices and wastewaters. However, it is doubtful whether such a remarkable rise in published output has significantly enhanced the knowledge about biosorption process, or aided any industrial

exploitation, which so often is the primary underlying principle for such investment and work [18, 19, 21]. Despite the incontestable progress made over decades of research, most of the biosorption studies are still conducted at a laboratory scale and involve (i) the characterization of a selected sorbent, which will sorb a given contaminant from solution, (ii) the study of the effect of physico-chemical parameters may have on biosorption and (iii) the use of metals. Considering that the majority of elements present in the periodic table are classified as metals, the potential number of 'original' research is most likely beyond comprehension, especially if coupled with the gigantic number of microbial species, strains and metabolites/derived substances. It is therefore expected that the output of publications related to biosorption shows no sign of decreasing and will be increased due to the continuing number of new journals, including those that are web based [18, 19].

It is also logical to infer that several technical and scientific issues should be solved in order to meet the industrial demands and bring the biosorption technology into commercialization. Based on this, several future perspectives can be made:

- Although a large number of biological materials are available, it is still essential to find and/or prepare more economic, efficient and selective sorbents.
- It is necessary to elaborate, improve and/or simplify the mathematical models used to describe the multicomponent systems.
- To achieve the best biosorption performance, it is crucial to identify the biosorption mechanism underlying relatively to the class of biosorbents used.
- To obtain the best biosorption performance, it is essential to identify the biosorption mechanism in relation to the general group of the selected biosorbent.
- Biosorption studies should also be conducted at a pilot or industrial scale and with multicomponent solutions or, if possible, real effluents and wastewaters. This will allow to understand the interactions between all the sorbents and the sorbate and thus optimize the biosorption process, promoting its future commercialization.
- Although there is a significant number of patents and publications available, the biosorption process has been so far mainly performed at a laboratory scale. Up-scale of the biosorption processes should be enhanced.
- In order to apply the biosorption technology at an industrial scale, economic analyses are necessary to estimate the overall cost of the sorbent and biosorption process.
- Additional attention should be paid to the application of biosorption technology in product separation, recovery and purification.
- The use of similar and universal evaluation methodologies allows to draw meaningful and universal conclusions [21].
- Eradicate the poor and misleading communications, and the use of loose terminology, which is associated with the great complexity of biosorption phenomena, has intricated the process of prioritizing fundamental scientific and commercial tasks and of creating clear information for the industry.

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Author details

Filomena Costa* and Teresa Tavares

*Address all correspondence to: filomenacpcosta@ceb.uminho.pt

University of Minho, Braga, Portugal

References

[1] Anastopoulos I, Kyzas GZ. Composts as biosorbents for decontamination of various pollutants: A review. Water, Air, and Soil Pollution. 2015;**226**:61-76. DOI: 10.1007/s11270-015-2345-2

[2] Abdi O, Kazemi M. A review study of biosorption of heavy metals and comparison between different biosorbents. J Mater Environ Sci. 2015;**6**(5):1386-1399 ISSN: 2028-2508

[3] Costa F, Tavares T. Bioremoval of Ni and Cd in the presence of diethylketone by fungi and by bacteria: A comparative study. International Biodeterioration & Biodegradation. 2017; **120**:115-123. DOI: 10.1016/j.ibiod.2017.02.018

[4] Costa F, Tavares T. Biosorption of nickel and cadmium in the presence of diethylketone by a *Streptococcus equisimilis* biofilm supported on vermiculite. International Biodeterioration & Biodegradation. 2016;**115**:119-132. DOI: 10.1016/j.ibiod.2016.08.004

[5] Ahmed S, Chughtai S, Keane MA. The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolites. Sep Purif Technol. 1998;**13**:57-64. DOI: 10.1016/S1383-5866(97)00063-4

[6] Chaudhuri D, Majumder A, Misra AK, Bandyopadhyay K. Cadmium removal by *Lemna minor* and *Spirodela polyrhiza*. International Journal of Phytoremediation. 2014;**16**:1119-1132. DOI: 10.1080/15226514.2013.821446

[7] Costa F, Tavares T. Sorption studies of diethylketone in the presence of Al^{3+}, Cd^{2+}, Ni^{2+} and Mn^{2+}, from lab-scale to pilot scale. Environmental Technology. 2017:1-13. DOI: 10.1080/09593330.2016.1278462

[8] Silva B, Costa F, Neves IC, Tavares T. Psychiatric Pharmaceuticals as Emerging Contaminants in Wastewater. 1st ed. Springer Cham Heidelberg New York Dordrecht London: Springer International Publishing; 2015. DOI: 10.1007/978-3-319-20493-2

[9] Costa F, Quintelas C, Tavares T. Kinetics of biodegradation of diethylketone by *Arthrobacter viscosus*. Biodegradation. 2012;**23**(1):81-92. DOI: 10.1007/s10532-011-9488-7

[10] Khan A, Singh VV, Dumar D. Removal of some basic dyes from artificial textile wastewater by adsorption on Akansh Kinari coal tabrez. J Sci Ind Res India. 2004;**63**(4):335-364 0975-1084 (online); 0022-4456 (print)

[11] Santos LH, Araújo AN, Fachini A, Pena A, Delerue-Matos C, Montenegro MC. Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. Journal of Hazardous Materials. 2010;**175**(1-3):45-95. DOI: 10.1016/j.jhazmat.2009.10.100

[12] Mak VWY, Chatzis I, Hudgins RR, Fayed ME. Removal of VOCs by sorption in fixed beds of popcorn. Canadian Journal of Chemical Engineering. 2004;**82**(1):194-197. DOI: 10.1002/cjce.5450820125

[13] Fan J, Sun Y, Li X, Zhao C, Tian D, Shao L, Wang J. Pollution of organic compounds and heavy metals in a coal gangue dump of the Gequan Coal Mine, China. Chinese Journal of Geochemistry. 2013;**32**:241-247. DOI: 10.1007/s11631-013-0628-0

[14] Costa F, Quintelas C, Tavares T. An approach to the metabolic degradation of diethylketone (DEK) by *Streptococcus equisimilis*: Effect of DEK on the growth, biodegradation kinetics and efficiency. Ecological Engineering. 2014;**70**:183-188. DOI: 10.1016/j.ecoleng.2014.05.009

[15] Costa F, Neto M, Nicolau A, Tavares T. Biodegradation of diethylketone by *Penicillium* sp. and *Alternaria* sp.—A comparative study biodegradation of diethylketone by fungi. Current Biochemical Engineering. 2015;**2**:81-89. DOI: 10.2174/2212711901666140812225947

[16] Seow TW, Lim CH. Removal of dye by adsorption: A review. International Journal of Applied Engineering Research. 2016;**11**(4):2675-2679 0973-4562

[17] The Environmental, Health and Economic Impacts of Textile Azo Dyes. Available from: https://www.researchgate.net/file.PostFileLoader.html?id=593cf7e2cbd5c26bf031fcab&assetKey=AS%3A503972613505026%401497167842679 [Accessed: 2017-08-03]

[18] Gadd GM. Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment. Journal of Chemical Technology & Biotechnology. 2009;**84**:13-28. DOI: 10.1002/jctb.1999

[19] Fomina M, Gadd GM. Biosorption: Current perspectives on concept, definition and application. Bioresource Technology. 2014;**160**:3-14. DOI: 10.1016/j.biortech.2013.12.102

[20] Volesky B, Biosorption of Heavy Metals. 1990. CRC Press, Boca Raton, FL. ISBN 978084 9349171

[21] Michalak I, Chojnacka K, Witek-Krowiak A. State of the art for the biosorption process—A review. Applied Biochemistry and Biotechnology. 2013;**170**:1389-1416. DOI: 10.1007/s12010-013-0269-0

[22] Sandrin TR, Maier RM. Impact of metals on the biodegradation of organic pollutants. Environmental Health Perspectives. 2003;**111**(8):1091-1101. DOI: 10.0000/www.ncbi.nlm.nih.gov/generic-8F48966398F4

[23] Abdulaziz M, Musayev S. Multicomponent biosorption of heavy metals from aqueous solutions: A review. Polish Journal of Environmental Studies. 2017;**26**(4):1433-1441. DOI: 10.15244/pjoes/67975

[24] Quintelas C, Costa F, Tavares T. Bioremoval of diethylketone by the synergistic combination of microorganisms and clays: Uptake, removal and kinetic studies. Environmental Science and Pollution Research. 2012;**20**(3):1374-1383. DOI: 10.1007/s11356-012-1055-1

[25] Nam I-H, Kim Y, Cho D, Kim J-G, Song H, Chul-M C. Effects of heavy metals on biodegradation of fluorene by a *Sphingobacterium* sp. strain (KM-02) isolated from polycyclic aromatic hydrocarbon-contaminated mine soil. Environmental Engineering Science. 2015;**32**(10):1-8. DOI: 10.1089/ees.2015.0037

[26] Said WA, Lewis DL. Quantitative assessment of the effects of metals on microbial degradation of organic chemicals. Applied and Environmental Microbiology. 1991;**57**:1498-1503

[27] Sandrin TR. Naphthalene Biodegradation in a Cadmium Cocontaminated System: Effects of Rhamnolipid, pH, and Divalent Cations [PhD Thesis]. Tucson, AZ: University of Arizona; 2000

[28] Benka-Coker MO, Ekundayo JA. Effects of heavy metals on growth of species of *Micrococcus* and *Pseudomonas* in a crude oil/mineral salts medium. Bioresource Technology. 1998;**66**:241-245. DOI: 10.1016/S0960-8524(98)00057-1

[29] Capone DG, Reese DD, Kiene RP. Effects of metals on methanogenesis, sulfate reduction, carbon dioxide evolution, and microbial biomass in anoxic salt marsh sediments. Applied and Environmental Microbiology. 1983;**45**:1586-1591

[30] Xie P, Hao X, Mohamad OA, Liang J, Wei G. Comparative study of chromium biosorption by *Mesorhizobium amorphae* strain CCNWGS0123 in single and binary mixtures. Applied Biochemistry and Biotechnology. 2013;**169**:570-587. DOI: 10.1007/s12010-012-9976-1

[31] Abu Al-Rub FA, El-Naas MH, Ashour I, Al-Marzouqi M. Biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions. Process Biochemistry. 2006;**41**:457-464. DOI: 10.1016/j.procbio.2005.07.018

[32] Pagnanelli F, Trifoni M, Beolchini F, Esposito A, Toro L, Vegliò F. Equilibrium biosorption studies in single and multi-metal systems. Process Biochemistry. 2001;**37**:115-124. DOI: 10.1016/S0032-9592(01)00180-7

[33] Aksu Z, Dönmez G. Binary biosorption of cadmium(II) and nickel(II) onto dried *Chlorella vulgaris*: Co-ion effect on mono-component isotherm parameters. Process Biochemistry. 2006;**41**:860-868. DOI: 10.1016/j.procbio.2005.10.025

[34] Mohapatra H, Gupta R. Concurrent sorption of Zn(II), Cu(II) and Co(II) by *Oscillatoria angustissima* as a function of pH in binary and ternary metal solutions. Bioresource Technology. 2005;**96**:1387-1398. DOI: 10.1016/j.biortech.2004.11.004

[35] Pradhan S, Rai LC. Biotechnological potential of *Microcystis* sp. in Cu, Zn and Cd biosorption from single and multimetallic systems. Biometals. 2001;**14**:67-74. DOI: 10.1023/A:1016607729691

[36] Chong KH, Volesky B. Metal biosorption equilibria in a ternary system. Biotechnology and Bioengineering. 1996;**49**:629-638. DOI: 10.1002/(SICI)1097-0290(19960320)49:6<629:AID-BIT4>3.0.CO;2-Q

[37] Michalak I, Chojnacka K. The application of macroalga *Pithophora varia* Wille enriched with microelements by biosorption as biological feed supplement for livestock. Journal of Science and Food Agriculture. 2008;**88**:1178-1186. DOI: 10.1002/jsfa.3195

[38] Roy AS, Kazarika J, Manikandan NA, Pakshirajan K, Syiem MB. Heavy metal removal from multicomponent system by the cyanobacterium *Nostoc muscorum*: Kinetics and interaction study. Applied Biochemistry and Biotechnology. 2015;**175**:3863-3874. DOI: 10.1007/s12010-015-1553-y

[39] Han X, Wong YS, Wong MH, Tam NFY. Effects of anions species and concentration on the removal of Cr(VI) by a microalgal isolate, *Chlorella miniata*. Journal of Hazardous Materials. 2008;**158**:615-620. DOI: 10.1016/j.jhazmat.2008.02.024

[40] Pulsawat W, Leksawasdi N, Rogers PL, Foster LJR. Anions effects on biosorption of Mn(II) by extracellular polymeric substance (EPS) from *Rhizobium etli*. Biotechnology Letters. 2003;**25**:1267-1270 ISSN: 0141-5492

[41] Filipović-Kovačević Ž, Sipos L, Briški F. Biosorption of chromium, copper, nickel and zinc ions onto fungal pellets of *Aspergillus niger* 405 from aqueous solutions. Food Technology and Biotechnology. 2000;**38**:211-216 ISSN: 1330-9862

[42] Ahuja P, Gupta R, Sabena RK. Zn^{2+} biosorption by *Oscillatoria anguistissima*. Process Biochemistry. 1999;**34**:77-85. DOI: 10.1016/S0032-9592(98)00072-7

[43] Kuyuca N, Volesky B. Accumulation of cobalt my marine alga. Biotechnology and Bioengineering. 1989;**33**:809-814. DOI: 10.1002/bit.260330703

[44] Tobin JM, Cooper DG, Neufeld RJ. Influence of anions on metal adsorption by *Rhizopus arrhizus* biomass. Biotechnology and Bioengineering. 1987;**30**(7):882-886. DOI: 10.1002/bit.260300711

[45] Vijayaraghavan K, Balasubramanian R. Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions. Journal of Environmental Management. 2015;**160**:283-296. DOI: 10.1016/j.jenvman.2015.06.030

[46] Sag Y, YAlcuk A, Kutsal T. Use of a mathematical model for prediction of the performance of the simultaneous biosorption of Cr(VI) and Fe(III) on *Rhizopus arrhizus* in a semi-batch reactor. Hydrometallurgy. 2001;**59**:77-87. DOI: 10.1016/S0304-386X(00)00143-2

[47] Fagundes-Klen MR, Ferri P, Martins TD, Tavares CRG, Silva EA. Equilibrium study of the binary mixture of cadmium–zinc ions biosorption by the *Sargassum filipendula* species using adsorption isotherms models and neural network. Biochemical Engineering Journal. 2007;**34**:136-146. DOI: 10.1016/j.bej.2006.11.023

[48] Vilar VJP, Loureiro JM, Botelho CMS, Boaventura RAR. Continuous biosorption of Pb/Cu and Pb/Cd in fixed-bed column using algae *Gelidium* and granulated agar extraction algal waste. Journal of Hazardous Materials. 2008;**154**:1173-1182. DOI: 10.1016/j.jhazmat.2007.11.060

[49] Martín-Lara MA, Blázquez G, Calero M, Almendros AI, Ronda A. Binary biosorption of copper and lead onto pine cone shell in batch reactors and in fixed bed columns. International Journal of Mineral Processing. 2016;**148**:72-82. DOI: 10.1016/j.minpro.2016.01.017

[50] Liu C-C, Wang M-K, Chiou C-S, Li Y-S, Yang C-Y, Lin YA. Biosorption of chromium, copper and zinc by wine-processing waste sludge: Single and multi-component system study. Journal of Hazardous Materials. 2009;**171**:386-392. DOI: 10.1016/j.jhazmat.2009.06.012

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