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Microbial Biosorption of Metals

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Preface

The word *biosorption* unites a biological entity with a physico-chemical process of sorption. Indeed, the biosorption of metal ions is a metabolism-independent metal accumulation event, which takes place at the cell wall by polysaccharides, associated molecules, and functional groups. It is an ubiquitous property of living or dead biomass and derived products, and is undoubtedly an important process in the environment. Since the early 80s of the previous century, the biosorption with biosorbents formulated from non-living biomass has also become recognized as a promising biotechnology for heavy metal removal from liquid waste streams. When we examine the ISI Web of Science, we can see that the number of journal papers published with *biosorption* and *metal* in their subject matter is at nearly 2700. Also the continuing increase in research published on biosorption can be seen, especially during the last decade. While there were 96 metal biosorption articles in 2000, the figure nearly doubled in 2005 to 178 articles. In 2009, the number of articles jumped to 393. These studies inspected biosorption from different angles—from (micro)biology and (bio)chemistry to process engineering points of view—and significantly contributed to elucidation of the biosorption phenomenon and its biotechnological potential. This book attempts to collect review articles which do justice to the multidisciplinary nature of biosorption studies. We are well aware of the fact that a single volume could not cover all the particular aspects one could think about in connection with biosorption. However, we do believe that it provides a solid summation of the present state of the biosorption art. At this point, it is our great pleasure to thank the team of authors whose fine contributions made this book possible.

Prague, Czech Republic

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Contents

Chapter 1
Microbial Biosorption of Metals—General Introduction

Pavel Kotrba

Abstract Discharge of waste contaminated with heavy metals and related elements is known to have an adverse effect on the environment and solving this problem has for long been presented as a challenge. Nowadays, continuing demand for and increasing value of high-tech metals and rare earth elements makes efficient recycling technologies of utmost importance. In solving these tasks, the biosorption—sequestration of heavy metals, radionuclides and rare earth elements usually by non-living biomass—can be a part of the solution.

Keywords Decontamination • Bacterial biosorbent • Fungal biosorbent • Algal biosorbent • Mechanism of biosorption • Modeling of biosorption

1.1 Brief View on Conventional Waste Stream Treatments

Industrialization has long been accepted as a hallmark of civilization. The Boulton and Watt steam engine, the synonym of industrial revolution, propelled huge changes in mining, metallurgical technology, manufacturing, transport and agriculture. Since then, progressive metallurgy and the use of metals and chemicals in numerous industries have resulted in a generation of large quantities of liquid effluent loaded with high levels of heavy metals, often as bioavailable mobile and thus toxic ionic species (Calderón et al. 2003; Peakall and Burger 2003; Gadd 1992a). Due to their elemental non-degradable nature, heavy metals always and regardless of their chemical form, pose serious ecological risk, when released into the environment. Not only is there the demand for cleanup of contaminated waste water to meet regulatory agency limits, but there is also increasing value of some metals which place a call for efficient and low-cost effluent treatment and metal recuperation technologies.

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Conventional procedures for heavy metal removal from aqueous industrial effluents involve precipitation, ion exchange, electrochemical methods and reverse osmosis. Another promising approach is solvent extraction. Conversion of metal ions to insoluble forms by chemical precipitation is the most common method, reducing the metal content of solution to the levels of mg l^{-1}. The cheapest precipitation technique relies on alkalization of the metal solution (usually with lime) to achieve formation of insoluble metal species, namely of hydroxides. Chemical precipitation could also be achieved by the addition of other coagulants, such as of potash alum, sodium bisuphite, sulphide or iron salts. Though it is cost effective; such precipitation lacks the specificity, produces large volumes of high water content sludge and has low performance at low metal concentrations. Although adsorption using activated carbon is generally expensive (and not suitable for many metal species), it is an efficient method for the removal of metallic mercury following chemical reduction (e.g., with hydrazine) of mercuric ions in heavily contaminated process waters.

Ion exchange employing manmade synthetic organic resins is the most common method. It becomes the method of choice especially for its capacity to reduce the metal contents to μg l^{-1} levels in relatively large volumes of effluent, some possibility to formulate metal-selective resin and well established procedures for metal recovery from and reuse of the ion exchanger. This method is, however, relatively expensive, which therefore makes the processing of concentrated metal solutions cost intensive. Precautions should also be taken to prevent the poisoning of ion exchanger by organics and solids in solution.

Electro-winning, employing electro-deposition of metals on anodes is popularly used for the recuperation of metals in mining and metallurgical operations as well as in electrical industries and electronics. Electrodialysis involves the use of ion selective semi-permeable membranes fitted between the charged electrodes attracting respective ions (in the case of metal cations, the anode compartment is smaller to concentrate the metal in). The main disadvantage of electrodialysis operation is clogging of the membrane by metal hydroxides formed during the process. Like electrodialysis, reverse osmosis and ultrafiltration employ semipermeable membranes which allow water to pass, while solutes, including heavy metals, remain contained in retentate. The advantages of membrane-based processes involve some selectivity of metal separation and tolerance to changes in pH. One disadvantage of membrane-based approaches is that they are cost intensive.

Reactive two-phase extraction complexing extractants specifically (or preferentially) dissolved in organic solvents has been suggested as another technological alternative (Schwuger et al. 2001). This approach may provide a viable method for the selective recuperation of metals, e.g., of platinum group metals from spent catalysts (Marinho et al. 2010). Suitable extractants for platinum involve organophosphorus compounds, aliphatic amines and ammonium quaternary salts. The main disadvantages of this process are the difficult recovery of metals from organic phase and the toxicity of extractants.

1.2 Bio-based Methods for Waste Water Treatment and Environment Restoration

The natural capacity of microrganisms, fungi, algae and plants to take up heavy metal ions and radionuclides and, in some cases, to promote their conversion to less toxic forms has sparked the interest of (micro)biologists, biotechnologists and environmental engineers for several decades. Consequently, various concepts for "bio-removal" of metals from waste streams and bioremediations of contaminated environment are being proposed, some of which were brought to pilot or industrial scale (Bargar et al. 2008; Macek et al. 2008; Muyzer and Stams 2008; Singh et al. 2008; Chaney et al. 2007; Sheoran and Sheoran 2006; Volesky 2004; Lloyd et al. 2003; Ruml and Kotrba 2003; Baker et al. 2000; Gadd 1992b; see also Chap. 2). The "bio" prefix refers to the involvement of biological entity, which is living organisms, dead cells and tissues, cellular components or products. The ultimate goal of these efforts is to provide an economical and eco-friendly technology, efficiently working also at metal levels below 10 mg l^{-1}. These are the features that living as well as dead biomass could be challenged for. There are generally three routes to follow considering "bio-removal" of metallic species from solutions. The first two rely on properties of living cells and involve active metal uptake—bioaccumulation (i.e., plasma membrane mediated transport of metal ion into cellular compartment) and eventual chemical conversion of mobile metal to insoluble forms. The later may occur in the cytoplasm, at the cell surface or in the solution by precipitation of metal ion with metabolites, via redox reactions or by their combination. The effectiveness of the process will depend on the (bio)chemistry of particular metal and on metabolic activity of eligible organism, which is in turn affected by the presence of metal ions. To this point, the use of metallotolerant species or physical separations of the production of metal-precipitating metabolite from metal precipitation in contaminated solution produce viable methods. For their importance in the treatment of industrial liquid streams as well as of the environmental pollution are some of these approaches discussed in Chap. 9. Several of them are to various extents dependent on or involve the metabolism-independent metal uptake event at the cell wall by polysaccharides, associated molecules, and functional groups. This metal sequestration capacity is commonly known as biosorption, which itself represents the third potent way of "bio-removal" of metals from solution.

Biosorption is a general property of living and dead biomass to rapidly bind and abiotically concentrate inorganic or organic compounds from even very diluted aqueous solutions. As a specific term, biosorption is used to depict a method that utilizes materials of biological origin—biosorbents formulated from non-living biomass—for the removal of target substances from aqueous solutions. Biosorption "traditionally" covers sequestration of heavy metals as well as rare earth elements and radionuclides or metalloids, but the research and applications extended to the removal of organics, namely dyes (Kaushik and Malik 2009; see also some examples with magnetic biocomposite biosorbents in Chap. 13), and biosorption is being proposed for the recovery of high-value proteins, steroids, pharmaceuticals and drugs (Volesky 2007).

Decades of biosorption research provided a solid understanding of the mechanism underlying microbial biosorption of heavy metals and related elements. It involves such physico-chemical processes as adsorption, ion-exchange, chelatation, complexation and microprecipitation. These depend on the type and ionic form of metal, the type of metal binding site available from microbial biomass, as well as on various external environmental factors (see Chap. 3). Accumulated knowledge resulted in the development of suitable modelling approaches comprehensively described in Chap. 4. When properly used, these models explain the equilibrium biosorption data, the kinetics in batch reactors and the dynamics in biosorption columns both for single and multimetal systems and provide a powerful tool for the design and development of the actual biosorption process. It should be noted here that it was due to a poor understanding of mechanisms and kinetics of AlgaSORB™ and AMT-Bioclaim™ processes commercialized in the early 1990s that hindered the adequate assessment of process performance and limitations, and thus the expected widespread industrial application of biosorption.

Biosorbents are derived from raw biomass selected for its superior metal-sequestering capacity. Investigated biomass types are of such diverse origins as bacterial, cyanobacterial, fungal (including filamentous fungi and unicellular yeasts), algal, plant or even animal (chitosan). This book covers development in major areas exploiting bacterial biomass (Chap. 5), fungal biomass (Chap. 6) and algal biomass (including macroalgae; Chap. 7) for the biosorption of heavy metal and radionuclides as well as for the sequestration of precious and rare earth elements (Chap. 8). It is noteworthy to add that the potential of plant-based biosorbents formulated from agricultural waste is attaining growing attention (Demirbas 2008; Sud et al. 2008; a few examples with magnetic biocomposite biosorbents are given in Chap. 13). The cheapest microbial biomass could be procured from selected fermentation industries as waste by-product or could be harvested from its natural habitat when it is produced in sufficient quantity there (e.g., marine macroalgae). Independent propagation of biomass under specific conditions optimizing its metallosorption properties is another option. Some efforts have been also devoted to modifications of yeast (Chap. 10) and bacterial (Chap. 11) cell walls through their genetic engineering, resulting in a surface display of particular amino acid sequences providing additional (even selective) metal-binding sites.

When derived from dead raw biomass featuring high metal uptake, the biosorbent for its practical application should exhibit some additional characteristics improving its stability and favoring hydrodynamic process conditions. To this end, biosorbent particle size, density and porosity, hardness, resistance to a broad range of physical and chemical conditions could be tailored by an appropriate immobilization method. Conventional strategies of biosorbent formulation from different types of microbial biomass are described in respective chapters as well as in Chap. 12. Chapter 13 further sets the biosorbent design forward to "smart materials", the magnetically responsive biocomposites improving biosorbents applicability by enabling their selective magnetic separation even from solutions containing suspended solids.

1.3 Future Thrusts in Biosorption

Compared with conventional or some biological methods for removing metal ions from industrial effluents, the biosorption process offers the advantages of low operating cost, minimization of the use of chemicals, no requirements for nutrients or disposal of biological or inorganic sludge, high efficiency at low metal concentrations, and no metal toxicity issues. The operation of biosorption shares many common features with ion-exchange technology and, despite shorter life cycle and less selectivity options, biosorbents could be considered direct competitors of ionex resins. The high cost of the ion-exchange process limits its application. Not all industries producing metal bearing effluents have financial resources for such sophisticated treatment and most opt only for basic decontamination techniques to meet regulation limits. The accumulated knowledge already provides a solid basis for the commercial exploitation of biosorption processes. Huge markets already exist (Volesky 2007) and they may even grow with progressively stricter legislation worldwide and increase demand on metal resources. Future efforts to improve selectivity and shelf life of biosorbents, further information on biosorption mechanisms and reliability and performance of biosorption models as well as more pilot scale demonstrations should bring convincing marketing arguments for large-scale applications. Biosorption also has the potential to find an industrial application in the future separation technologies with renewable biosorbents complementing conventional methods in hybrid or integrated installations.

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Chapter 2
Potential of Biosorption Technology

Tomas Macek and Martina Mackova

Abstract Heavy metal removal from inorganic effluent can be achieved by conventional treatment such as chemical precipitation, ion exchane or flotation, however each treatment has its limitation. Recently, sorption, namely biosorption has become one of the alternative treatments. Basically, sorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and substance becomes bound by physical and/or chemical interactions. Due to large surface area, high sorption capacity and surface reactivity of sorbents, sorption can be utilized as low-cost alternative to conventional processes. For example, materials locally available in large quantities such as natural materials, living or dead biomass, agricultural waste or industrial byproducta can be used as biosorbents with quite little processing. This chapter discusses the significance of the heavy metal removal from waste streams and provides brief oveview of the potential of biosorbents and biosorption technology. Considered are various aspects of utilization of microbial and plant derived biomass in connection with biosorption and the possibility of exploiting such material for heavy metal removal form solutions.

Keywords Heavy metals • Biomass • Biosorption • Biosorbent • Bioavailability

2.1 Significance of Metal Recovery—Industrial and Environmental View

Heavy metal pollution is one of the most important environmental problems today. Various industries produce and discharge wastes containing different heavy metals into the environment, such as mining and smelting of metalliferous ores, surface

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