Review

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Minireview

The Advent of Biotechnology in Resource Technology

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This review is part of the 2021 submitted dissertation entitled "Tailor-made metal- and metalloid-binding peptides – From the identification of phage displayed peptides to their provision for biosorbent development" submitted by Dr. Robert Braun [1].

Abstract: The usage of biotechnological molecules and processes is an indispensable part of the resource technology research. The development of novel biomolecules therefore needs to be adapted to the existing applicational conditions and biological processes are to be examined. Novel biosorbents may not only contribute to future applications but can be of further used, *e.g.* to better understand the interaction of known metal- and metalloid-interacting biological molecules and materials. This review highlights biotechnological approaches published so far for bioremediation as well as metal recovery with a special spotlight on cobalt, nickel and arsenic.

Keywords: biomining; bioleaching; biosorption; bioaccumulation; biomolecules; cobalt; nickel; arsenic

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1. Challenges for mining & society – Element scarcity, decreasing ore grades and ever increasing contamination

Mining and the provision of resources as metals, metalloids and rare earth elements are of outmost importance for the global population. However, the mining industry is confronted with decreasing ore grades while at the same time, energy consumption is steadily increasing for the commercial exploitation of valuables, *e.g.* the average ore grade of global copper mines decreased by 25 % in the last ten years, whereas the energy consumption increased by 46 %, compared to 30 % increase in production [2]. Decreasing ore grades combined with increased production furthermore led to increased waste production and to the contamination of air, water and soils with heavy metals [3]. This pollution with toxic heavy metals [4] is mainly caused by effluent waters from mines, landfills, factories and industrial metal processing [5]. Although some heavy metals are essential for biological processes [6], hazardous and harmful biochemical effects are described for most heavy metals even in low concentrations [7].

Through increasingly strict environmental legislation, mining companies are now being forced to improve their environmental performance by decreased waste production, waste collection and recycling, and by neutralization of toxic pollutants [8,9].

At the same time, the emergence of new technologies, the development towards "low carbon technologies" and market participation of an growing part of the world population leads to drastically increased global demand for high-tech elements *e.g.* rare earth elements (REE), gallium, germanium and indium [10,11]. Element scarcity is further driven by the global distribution of natural resources. Half of world's REE reserves are located in the People's Republic of China [12]. 89 % of world's production of platinum group metals (PGM) is generated in South Africa. 40 % of world's cobalt production is located in the Democratic Republic of Congo and 90 % of niobium is produced in Brazil, for example [13]. Therefore, geopolitical tensions and trade disputes are critical issues that affect the satisfaction of world's resource demand [14]. Since 2011, the European Commission publishes a list of critical raw materials with high importance and a high supply risk. In 2023, 34 elements (compared to 14 elements in 2011) are listed as critical, including all light and heavy rare earth elements, all platinum group metals (PGM, ruthenium, rhodium, palladium, osmium, iridium, platinum) as well as gallium, germanium and vanadium [15].

Already long before, the transformation of mining industry towards the increasing use of bio-based processes had begun, called biomining.

2. Biomining

Biomining is defined as the collection of biological processes for the extraction of metals and valuables from primary and secondary sources [16]. Compared to the history of mining, biomining is a new approach for the improved mineral exploitation of primary and secondary sources of minerals. It can be used for the remediation of contaminated soils and waters and allows the mining of minerals, which previously could not be profitably extracted. Biomining can further be used for the extraction of minerals from secondary resources, *e.g.* from landfills, mining dumps and tailing ponds, which are needed as long-term storage for processed tailing streams of conventional mining and are highly toxic for the surrounding environment. Other sources of secondary resources are also solid and liquid wastes from end-of-life electronic consumer goods that contain high concentrations of valuable elements [11].

Another reason for the advent of biotechnology in mining is, that the application of physicochemical processes for the recovery of heavy metals and the environmental remediation from mining residue *e.g.* tailing ponds is both expensive, ineffective and not profitable. Chemical precipitation, coagulation, ion exchange, electrochemical methods and the adsorption via activated carbon are mainly used methods in traditional mining, but suffer from ineffectiveness especially for low concentrated heavy metals. Furthermore, the processing of large amounts of waste and sludge and the reusability of *e.g.* activated carbon difficult is limited [17].

Since the 1950s, biomining is part of commercial mining, when for the first time, the auxotrophic bacterium *Thiobacillus ferrooxidans* was used in mining, leading the path for broader application of bioleaching in mining [18].

3. Bioleaching

The term bioleaching describes the transformation of an insoluble metal compound into a water-soluble form metabolic activity of bacteria (direct bioleaching) or metabolic compounds (indirect bioleaching) [5]. Mostly, acidophilic, chemolithoautotrophically growing bacteria or archaea are used for the oxidation of metal sulfide compounds. Ionic Fe(III) is provided by the organisms by oxidizing Fe(II) ions. 'Acid-insoluble' minerals (*e.g.* pyrite FeS_2) and 'acid-soluble' minerals (*e.g.* sphalerite ZnS) differ in the following oxidation steps. For 'acid-insoluble' minerals, the mineral sulfur moiety is oxidized to thiosulfate (thiosulfate pathway) and further oxidized to sulfuric acid by sulfur-oxidizing acidophiles. The resulting ionic Fe(II) is oxidized again by iron-oxidizing acidophiles. 'Acid-soluble minerals' are transformed by oxidation of the sulfur moiety to elemental sulfur mediated by Fe(III) ions and H^+ via several polysulfides (polysulfide pathway). The sulfur accumulates or is further oxidized by sulfur-oxidizing acidophiles providing H^+ for the aforementioned step [16,19]. The most important organisms for chemolithoautotrophic bioleaching are *Acidithiobacillus ferrooxidans* (which was formerly described as *Thiobacillus ferrooxidans* mentioned above) and *Leptospirillum ferriphilum* [20].

Bioleaching is nowadays a well-established niche technology [16], which is mainly used for heap and dump bioleaching of polymetallic ores and low-grade copper (in 2010 38 % of leached copper from bioleaching), but is furthermore applied for gold, cobalt, nickel, zinc and uranium. However, as gold cannot be oxidized, the surrounding refractory ore is oxidized to access the gold (biooxidation). Bioleaching is mostly used for sulfide ores, but laboratory approaches for silicate and oxide ores by anaerobic bioleaching [21-23] and the usage of heterotrophic microorganisms [24,25], requiring organic carbon, have been shown. Indirect bioleaching with organic compounds produced by heterotrophic bacteria *e.g.* citric acid, glutamic acid or metal-complexing molecules as siderophores is another promising approach to extend or replace sulfuric acid in bioleaching [5]. Alternatives for chemolithoautotrophically bioleaching have to be found, because like traditional metallurgical leaching, huge tailing ponds with highly acidic liquid waste are needed for large-scale heap or dump bioleaching. This acid mine drainage has a heavy environmental impact [26,27].

Recently, bioleaching of solid waste has been accomplished for the recovery of residues from electric industry, circuit boards and spent catalysts but also from industrial waste as ashes power stations utilizing acidophilic, autotrophic microorganisms and/or enzymatic reduction [28].

4. Biosorption and bioaccumulation

Bioleaching mainly includes processes for metal compound dissolution, whereas the term biosorption describes the passive binding and concentration of specific molecules, which may not necessarily be metal ions, by living cells and non-living bio-derived materials as biomass, biomolecules and proteins. Bioaccumulation describes the accumulation of molecules by active transport and cellular uptake in living organisms for further utilization in cellular processes as enzyme catalysis or signaling by mostly ATP-driven processes [5,29-31]. Both, biosorption and bioaccumulation, are natural processes, that can be observed most commonly in extreme and/or anthropogenic environments as mining regions [32] and are currently technologically improved and exploited.

Current hydrometallurgical processes for the recovery of metal and metalloid ions are either ineffective for the recovery of very low concentrated metals and/or cause secondary toxic chemical sludge, that requires further treatment [17,33]. The main advantage for usage of biosorptive materials for the recovery of heavy metals therefore lies in the treatment of with low concentrated heavy metal ions contaminated water bodies, while not causing additional toxic side products. However, selective binding of individual heavy metals would open additional fields of application for commercial recovery of valuables.

Biosorption has been performed with manifold types of biomass, including bacteria, yeast, algae, fungi and plants and almost all metals have been examined regarding their biosorption potential [34-37]. Industrial organic waste products are cheap and available in large dimensions, therefore organic waste from rice [38], and leaf biomass [39] have been used for the recovery of heavy metals. Besides organisms, metabolic products as biopolymers have been examined for their biosorption potential, *e.g.* chitosan, polyglutamic acid, teichoic acid, lipopolysaccharides and extracellular polymeric substances [17, 40-44]. Recently, by means of genetic engineering, MerP proteins involved in the binding and transport of mercury from *Pseudomonas* sp. and *Bacillus cereus* have been heterologously expressed and produced in *E. coli* and characterized in terms of their biosorption capacity for different heavy metal ions [45,46]. Biosorptive processes can be performed with either living or dead, free or immobilized, raw or pretreated, wild-type or genetically modified cells.

Whereas most scientific publications on biosorption deal with the removal of major pollutants as lead, mercury, cadmium and radionuclides, it has also been described for the recovery of precious elements as rare earth elements [47-50], gold [30,51] and many organic compounds as phenols and dyes [52].

The underlying mechanism of metal sequestration is based on the interaction of functional groups provided by biomass with the metal ions. Metal ion-interaction surface functionalities can include hydroxyl, carbonyl, carboxylate, dioxide, nitric oxide, sulfhydryl (thiol), sulfonate, thioester, amine, amide, imine, imidazole, phosphonate and phosphodiester groups depending on the biosorbent [17,53]. Biosorption of metals mainly occurs by ion exchange and coordination/complexation. Bioaccumulation requires ATP-driven processes that allow living cells to transport metal ions across the cell membrane and further processing for reduction and precipitation [37]. Precipitation, mostly performed through active processes, has been described as a biosorptive process independent from the cellular metabolism, too [54].

Besides equilibrium time, biomass concentration and temperature, biosorption is mainly dependent from the pH value. For cationic metal ions in general, higher metal recovery is achieved at neutral or alkaline pH and increases with increased pH, due to more negatively charged binding sites exposed on the biomass and in correlation with the deprotonation of carboxylic groups [55].

Moreover, the pH value influences the binding site dissociation and speciation chemistry of the respective metal, its hydrolysis and complexation by organic and inorganic ligands, redox reactions and precipitation [35]. The metal speciation is of high importance and often limits the recovery to suitable pH ranges, however *e.g.* biosorption at different pH values of both positively charged Cr(VI) and negatively charged reduced Cr(III) chromium species with seaweed has been published [56].

Modifications of biomass for increased biosorption have been published including crosslinking, substitution, oxidation [57] and variation of physicochemical properties as heat treatment [58]. Increased sorption capacity has been described for both acidic and alkaline pre-treatment of biomass with organic and inorganic substances, *e.g.* with NaOH for Zn(II) biosorption [59], HCl for Ni(II) removal [60] and with polyacrylic acid for biosorption of Cd(II) [61]. These modifications target the surface-exposed functional groups and their contribution to the biosorption behavior, as shown for the accumulation of REE by esterification and amidation of surface-exposed carboxyl groups of *E. coli* [50].

The metal-loaded biosorbents can be used for catalytic purposes or the recovered metals can be desorbed for further usage. However, often the amount of hazardous materials needed for desorption is as high as for traditional processes, reversing the benefits of biosoprtion, alternatively pyrometallurgical processes have been applied for recovery of metals bound to biosorbents [53]. Alternatively, the usage of loaded biosorbents as effective and low-cost catalysts offers advantages for removal of hazardous substances from industrial waste, as shown for the degradation of 2-chlorophenol with Ni(II)-loaded biosorbent [62].Though effective recovery could be shown for many metals and metalloids, biosorption remains highly dependent on the biosorbent material and the surrounding physicochemical properties, the effects of competing ions and the ionic state and solution chemistry of the respective metal ion [35,63].

Although selective biosorption processes have been described, the selective biosorptive removal and/or recovery of pollutants remains challenging and is mostly unsuccesful [64]. The binding mechanisms are often complex and include adsorption, chelation and ion exchange and membrane-driven diffusion processes. Several functional groups and biological molecules are involved in the metal ion binding. For bioaccumulation, ion exchange was shown to be the dominating mechanism for metal ion interaction, however the contribution of the individual functional groups differs for each biosorbent [65]. Metal ion sequestration is the result of the interaction of different functional groups of the involved biomolecules [66]. The description of the underlying binding mechanism, the identification of the responsible functional groups, their contribution and structure is therefore complicated. For individual biosorbents, the amount of involvement has been determined, as shown for a species of the blue-green algae *Spirulina*, where blocking of carboxyl and phosphate groups led to 61 % loss of Cr(III) ion uptake capacity. Blocking of hydroxyl groups resulted in 16 % loss of uptake capacity, indicating the major role of carboxyl and phosphate groups for the metal sequestration in this biosorbent [67].

The targeted removal of specific metal ions has been made possible by the introduction of genetic engineering and the construction of artificial biosorbents and organisms for bioaccumulation of contaminants. Whereas bioaccumulation has long been used as an indicator for polluted environments [68-71], the combination with genetic engineering opened larger fields of application [6]. Furthermore, the construction and usage of genetically engineered biosorbents allows for a more detailed insight into the involved processes, functional groups and molecules. Suitable metal-binding ligands for either intracellular expression or surface display are *e.g.* phytochelatins and metallothioneins. Phytochelatins and metallothioneins were discovered in animals [72,73] and in plants [74,75], and are rich in cysteines [73,76]. Whereas phytochelatins are enzymatically synthesized proteins requiring the intracellular expression of a phytochelatin synthase enzyme [72], metallothioneins are genetically encoded polypeptides.

Genetically modified organisms for usage as biosorbent are constructed by display of proteins on the cell surface. For Gram-negative bacteria, cell surface display is most often described for fusion proteins with outer membrane proteins and porins (Omp, LamB), fimbriae, pili, nucleation proteins, surface layer proteins and the maltose-binding protein [6,77]. Different metallothioneins and polyhistidines were displayed on the porins LamB [78-80], OmpA [81], OmpC [82] and on surface layer proteins [83]. Display of poly-histidine peptides has also been described as fusion to Gram-positive *Staphylococcus* sp. anchor protein SpA [84]. In yeast, metallothioneins and polyhistidine peptides have been expressed as fusion proteins with agglutinin for cell surface display [85-87].

The usage of phytochelatins in genetically engineered organisms required the expression of a phytochelatin synthase, which was published for bacteria [88-90], yeast [91,92] and transgenic plants [93]. The bacterial cell surface display of phytochelatin-derived peptides is an alternative biosorption approach utilizing phytochelatins [94]. Besides metallothioneins and phytochelatins, other known metal-binding domains have been utilized for biosorption purposes, as the bacterial molybdenum transport protein ModE [95] and naturally occurring lanthanide binding tags as calmodulin [96] for recovery of REE [97-99].

The usage of genetically engineered organisms and molecules in biosorption is however not limited to the display of naturally occurring biological molecules. Directed evolution approaches as phage display allow the identification of novel target-specific binding sequences, which may be utilized for biosorption and bioaccumulation purposes. Artificial lead-binding peptides have been identified using phage display and were utilized as OmpC fusion proteins for the selective adsorption of lead with whole cells [100,101]. Yeast surface display has been published for Ni(II) adsorption with artificial peptides, which have been identified using phage display beforehand [102]. Another approach was published in 2015 by Yang *et al.* Adsorption of chromium was accomplished directly onto phage, displaying chromium-binding peptides previously identified via phage display [103].

Next to biosorption and bioaccumulation, plenty of other bio-based methods for the recovery and/or removal of heavy metal ions exist but will not be discussed here in detail. Most of these methods are either variations or extensions of the above described processes, *e.g.* by combination of bioaccumulation with redox-active enzymes for the formation of minerals in the so-called biomineralization [104,105], which has successfully been applied for the recovery of metals from ores and concentrates [106]. The process of bioreduction [107,108] has *e.g.* been described for the recovery of gold but may also be combined with biosorption for the removal of toxic heavy metal species [109]. Other processes include bioprecipitation [110,111], bioimmobilization [112], biocoagulation [113], bioflocculation [114] and bioflotation [111]. Also, the concepts describe both biological and technical processes and may overlap and partly refer to the same underlying processes.

5. Biosorption and bioaccumulation of Cobalt and Nickel

Biosorption of cobalt and nickel ions in solution to naturally occurring organisms has been described for bacteria [115,116], yeast [117], algae [118-120] and fungi [121,122]. Waste plant biomass as lemon peel has been used for biosorption [123] as well as living plants as *Berkheya coddii*, a well-described hyperaccumulator [124]. Even animal biomass as crab shell has been examined for its cobalt biosorption [125]. Furthermore, artificial biosorptive materials consisting of biological molecules linked to inorganic carriers, as BSA-coated bubbles have been described [126].

By means of genetic engineering the natural adsorption and uptake of nickel and cobalt ions could also be increased. Compared to biosorption processes with naturally occurring organisms, these engineered biosorbents/-accumulators possess increased metal ion selectivity and allow for a better understanding of the underlying binding mechanisms due to their defined nature. Nickel and cobalt bioaccumulation with genetically modified organisms has been mainly achieved by heterologous expression of known nickel cobalt transporters (NiCoT) [127] and in combination of intracellular expression of metallothioneins [65,128,129]. Although many NiCoT proteins are known, the amino acids involved in the interaction with the metal ions have not been described. However, the conserved amino acids in the nickel permease NixA of *Helicobacter pylori* have been described. Interestingly, next to aspartic acid, glutamic acid and histidine, which are known to be good nickel-binders [130], defined positions of serine, threonine, phenylalanine and asparagine were found to be crucial for NixA mediated uptake of nickel [131,132]. Though, these amino acids may not be directly involved in the interaction with the metal ion, but may be required for the conformation or stability of NixA. The main functional groups of the nickel cobalt transporters involved in the nickel uptake mediated by NixA of *Helicobacter pylori* and NisA of *Staphylococcus aureus* were found to be carboxyl groups over hydroxyl groups in experiments, where nickel uptake was measured after selective blocking of the respective functional group [129].

The application of phage display for discovery of nickel-binding peptides led to the identification of the peptide sequences GLHTWATNLYHM, HAVSPTLPAYSK, SGVYKVAYDASR, which show similarity to known nickel-binding proteins. The surface display of the acquired peptides either in combination or separately fused to agglutinin Aga2 of *Saccharomyces cerevisiae* led to increased biosorption capacity of the genetically modified yeast [102].

6. Arsenic and its biotechnological removal strategies

Arsenic is a ubiquitous, toxic metalloid, which exists in many minerals. It is released through both natural and anthropogenic activities [133], *e.g.* by copper smelting plants [134], which contaminates natural waters worldwide [135] and is even accumulated in plants as rice [135]. Due to its ubiquitous occurrence in drinking water and the dietary food intake in many regions worldwide, the population of many countries as Taiwan, Argentina, Chile, Mexico, India and Bangladesh are exposed to high levels of arsenic [137]. Therefore, it has been ranked by different governmental agencies worldwide as most important and prioritized hazardous substance, *e.g.* by the United States Agency for Toxic Substances and Disease Registry (ATSDR) [138]. Its toxicity arises from inorganic arsenate ($HAsO_4^{2-}$) mimicking phosphate (HPO_4^{2-}). Arsenate thus competes for phosphate transporters and inhibits phosphate-metabolizing enzymes, including essential metabolic processes like the oxidative phosphorylation to regenerate adenosine-5'-triphosphate (ATP) [139]. Due to its ubiquitous occurrence, nearly all living organisms have developed systems for arsenic detoxification [140]. The oxidation states of arsenic (-3, 0, +3, +5) depend on surrounding pH and redox potential. The biologically most important and most occurring forms of arsenic are arsenate As(V) ($H_2AsO_4^-$ and $HAsO_4^{2-}$) and arsenite As(III) ($H_3AsO_3^0$ and $H_2AsO_3^-$) as the oxyacids arsenic and arsenous acid [140,141]. Methylated arsenic species are the result of detoxification processes of living organisms but may not necessarily decrease toxicity but contribute to adverse effects [142].

Conventional methods for treatment of arsenic-containing waters include sulfide and hydroxide precipitation, coagulation and the adsorption of arsenic to iron and aluminium hydroxides, oxidation of As(III) by hypochlorite, permanganate and hydrogen peroxide. However, these methods include the formation of toxic side products and are limited for low-concentrated arsenic [143-145]. Whereas some progress has been made in the development of new, conventional sorbents, *e.g.* by combination of iron oxide and activated carbon [146], biosorption and bioaccumulation of arsenic is becoming increasingly important and has been described for manifold biological materials, *e.g.* for biopolymers as chitosan [147] and for biomass from bacteria [148,149], yeast [150], algae[151], plants[144,152-157], fungi [158,159] and animals [160]. Activation of biomass by alkali or acid treatment has been described as well as the production of biocomposites by treatment of biomass with organic compounds and metal oxides [161], *e.g.* for methylation of the biomass to enhance the sorption capacity [150]. The major mechanisms for As sorption by biomass are electrostatic interactions, hydrogen bonding, ion exchange and interactions with ionizable functional groups as amino groups [161]. Due to the individual properties of (modified) biomass and biocomposites, general industrial applications are yet to be shown. Treatment of biomass, which previously resulted in increased sorption capacity may show adverse effects on different materials, hindering the comparison for economic feasibility, as well. Regeneration of biosorbents is closely linked to the underlying sorption mechanism, therefore desorption is often complicated and can result in limited usability. Furthermore, as sorption of As is mostly unspecific, competitive anions decrease the sorption of arsenic species [147].

The development of artificial biosorbents by combination of inorganic carrier materials with biosorptive materials is an interesting approach and may lead to increased sorption capacity and to better reusability and adaption to established processes, as shown for the coating of ceramic alumina with chitosan [162]. Despite missing conventional removal strategies, selective biosorption and recovery of oxyanions as arsenite, arsenate, borate, bromate, molybdate, selenite, selenate and vanadate is rarely described because of their complex ionic state and solution chemistry [163].

Increased selectivity and better understanding of the involved biomolecules, functional groups and binding mechanisms can be achieved by bioaccumulation approaches with genetically engineered organisms. Up to this day, arsenic transport and detoxification systems have been described in nearly all living organisms [140]. In environments with high heavy metal concentrations, organisms could be identified, that are able to withstand arsenic concentration of ~ 200 mM [164]. Families of arsenic transporters have been described in both pro- and eukaryotic organisms [165]. Whereas the major uptake system of arsenic in prokaryotes is the ubiquitous *ars* operon including a arsenite-translocating ATPase form by ArsA and ArsB [166], the transport in eukaryotic cells is achieved by proteins of the MRP (multidrug resistance-associated protein) group of transport ATPases [165] of which Ycf1p of *Saccharomyces cerevisiae* is the best-described [167]. At neutral pH arsenic occurs as $As(OH)_3$, resembling organic molecules such as glycerol. Therefore transport of arsenite is also performed by aquaporins and aquaglyceroporins [168-170]. The similarity to essential molecules is also the reason why arsenate is transported by carrier proteins of the phosphate uptake system [171,172]. Furthermore, the intracellular enzymatical reduction of arsenate has been described [173]. Whereas common in prokaryotes, the only identified eukaryotic arsenate reductase is Acr2p of *S. cerevisiae* [174]. Biomethylation of arsenic to lower the toxicity by forming methylarsonate, monomethylarsonous acid, dimethylarsinic acid and dimethylarsonous acid has also been described, involving both reductases and methyltransferases [175].

Conserved amino acid residues, that interact with arsenic have been described in membrane transport proteins, reductases, phosphatases, thioredoxins, DNA repair enzymes, zinc-fingers and metallothioneins and the binding and coordination of arsenic has been solely described for cysteine [139,176-179]. Histidine, which is involved in the binding of metals as Fe, Zn, Co and Ni, has not been shown to interact with arsenic [139]. Recently, a new family of periplasmic-binding proteins of *Rhizobium* sp. has been described, where conserved tyrosine residues were part of the binding pocket, next to cysteine [180]. Conserved arginine residues have been described to be part of the oxyanion binding pocket of ArsC in *E. coli* [181] and conserved histidines were found at fixed positions in the ArsA ATPase of *E. coli* [182]. However, these conserved residues are not involved in the catalytic coordination of arsenic, but in the structural coordination or the signal transmission between the catalytic and allosteric sites.

Binding and accumulation of arsenic by heterologously produced proteins or enzymes, involved in the synthesis of arsenic-binding biomolecules has been described mainly for the expression of phytochelatin synthases in yeast [89,91,183,184] and metallothioneins in bacteria [185-187]. The co-expression of aquaglyceroporins [89,188], phosphate [189] and sugar transporters [188] has been shown to further increase arsenic uptake of engineered cells. Metalloregulatory proteins as ArsR, a transcriptional repressor in *E. coli*, and enzymes for arsenate reduction were both deleted [190], overexpressed [191,192] and combined with the overexpression of aquaglyceroporins in more complex approaches for increased bioaccumulation of arsenite [190]. Cysteine has so far been the only amino acid, that has been described for coordination of arsenic in both metallothioneins and phytochelatins [193-195].

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