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Microorganism mediated biosynthesis of metal chalcogenides; a powerful tool to transform toxic effluents into functional nanomaterials

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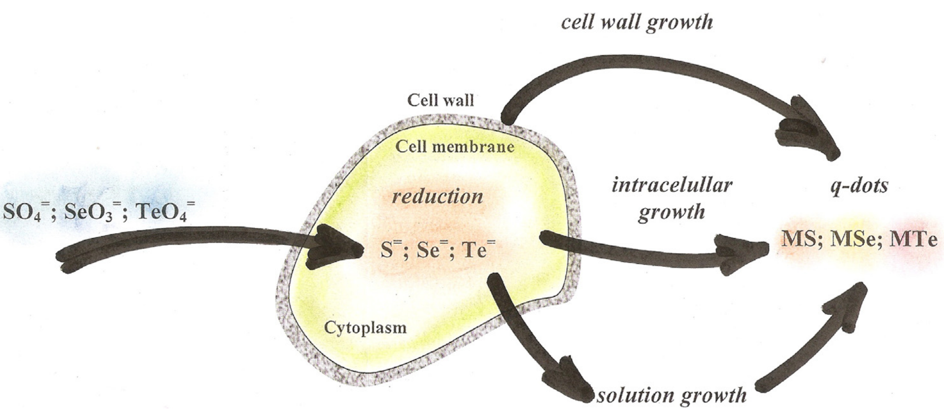
HIGHLIGHTS

- Removal of heavy metals by living matter is feasible trough biosorption and bioaccumulation
- Algae, fungi, bacteria and yeasts can synthesize CdS, CdSe and CdTe Q-dots
- Encapsulation of microorganisms in mineral gels provides building blocks for reactor design.
- Depletion of Cd with production of Q-dots can be achieved with modular bioreactors with entrapped cells

GRAPHICAL ABSTRACT



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ABSTRACT

Cadmium contained in soil and water can be taken up by certain crops and aquatic organisms and accumulate in the food-chain, thus removal of Cd from mining or industrial effluents – i.e. Ni-Cd batteries, electroplating, pigments, fertilizers – becomes mandatory for human health. In parallel, there is an increased interest in the production of luminescent Q-dots for applications in bioimaging, sensors and electronic devices, even the present synthesis methods are economic and environmentally costly. An alternative green pathway for producing Metal chalcogenides (MC: CdS, CdSe, CdTe) nanocrystals is based on the metabolic activity of living organisms. Intracellular and extracellular biosynthesis of can be achieved within a biomimetic approach feeding living organisms with Cd precursors providing new routes for combining bioremediation with green routes for producing MC nanoparticles. In this mini-review we present the state-of-the-art of biosynthesis of MC nanoparticles with a critical discussion of parameters involved and protocols. Few existing examples of scaling-up are also discussed. A modular reactor based on microorganisms entrapped in biocompatible mineral matrices – already proven for bioremediation of dissolved dyes – is proposed for combining both Cd-depletion and MC nanoparticle's production.

1. Introduction

Industrialized civilization left the legacy of global-scale pollution of air, seas and land; this undesired side effect limits the present and future health of the environment as a whole. On recent decades civilization

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evolved developing concrete policies towards the recovery of the damaged environments and the incorporation of sustainable resources management. Nowadays, those main goals merge in novel approaches for remediation and waste treatment that convert undesired pollution agents in valuable products. To make real this two-fold win scenario, the mandatory chemical transformations involved in the process must be green and economically feasible. Biologically driven process can satisfy those requirements as they offer exquisite biochemical pathways, both in terms of product specificity and yield. One exciting example of this approach lies in the microorganism mediated formation of functional nanoparticles from heavy metal loaded effluents. In contrast with other molecular pollutants that can be totally biodegraded, heavy metals can only be treated in terms of separation through chemical transformation, as for example reduction to metal, precipitation forming insoluble less toxic solid phases, such as carbonates, phosphates or sulfides.

Physico-chemical methods for remediation of waste contaminated with heavy metals present several disadvantages due to the high requirement of reagents, most of them with high negative environmental impact. In this scenario the use of plants, plant extracts or microorganisms, such as bacteria, fungi, yeasts and algae to treat toxic pollutants is envisaged as an affordable technology inherently biocompatible (Mittal et al., 2013; Malik, 2004; Boopathy, 2000; Gadd, 2010). Since microorganisms cannot decompose heavy metals, detoxification strategies are based on the bioavailability minimization. One of those strategies is biosorption, or the ability of microorganisms to reversibly bind heavy metal ions at the cell surface. The functional groups present in the cell wall of algae, fungi and bacteria include carboxyl, amine, phosphonate and hydroxyl groups which play an important role in metal complexation (Volesky and Holan, 1995; Rangabhashiyam et al., 2014). In most cases metal biosorption follow a Langmuir or Freundlich isotherm and a pseudo second order kinetics, being independent on the cell metabolism (Srivastava et al., 2015; Febrianto et al., 2009). This enables the use of dead cells and cell fragments – i.e. bacterial S-layers (Allievi et al., 2011) – with the advantage of low cost procedures while it doesn't retain metabolic activity, thus being independent of the effluents toxicity and nutrient supply. A more challenging approach for remediation is bioaccumulation, or the uptake of metal ions by metabolically active organisms. Within this scheme heavy metals can be biosorbed by living organisms (passive uptake) and enter into the cell through the cell metabolic cycle (active uptake) (Malik, 2004). Therefore, bioaccumulation in living microorganisms opens the gate for complex and eventually relevant chemical transformations.

The specificity of metal uptake is enhanced when particular functional groups are present at the cell surface, such as siderophores chelates that reduce Fe^{3+} into Fe^{2+} being actively transported inside a bacterial cell (Neilands, 1995) or metallothioneins from eukaryotic cells synthesized under heavy metal stress which can complex Cu^{2+}, Zn^{2+}, or Cd^{2+} (Nies, 1992). Once at the surface, metal ions can remain bound to the biomolecules on the cell wall or they can suffer active transport towards the cytoplasm where they can be transformed to less harmful compounds or just accumulated in cellular vacuoles. Microorganisms present several specific and non-specific pathways to chelate, methylate, reduce or oxidize ionic compounds. Among others, Sulfate Reducing Bacteria (SRB) (Muyzer and Stams, 2008) are able to use sulfate as electron acceptor, producing sulfide. Other metalloid oxyanions, such as SeO_3^{2-} and TeO_3^{2-} can be also reduced to insoluble Se^0 and Te^0, respectively (Chung et al., 2006; Kim et al., 2013; Rajwade and Paknikar, 2003; Fellowes et al., 2013).

In the presence of metallic ions, the formation of sulfide, selenide or telluride leads to precipitation of the corresponding metal chalcogenides opening doors for new green routes for the obtainment of valuable nanoparticles, such as Q-dots. The discovery of magnetotactic bacteria was a milestone; (Blakemore, 1975) these bacteria orientate towards a magnetic field thanks to the intracellular synthesis of monodisperse magnetite (Fe_3O_4) or greigite (Fe_3S_4) nanocrystals within the magnetosome (Bazylinski and Frankel, 2004). The well-documented biosynthesis of nanocrystalline functional materials triggered biomimetic and bioinspired attempts to achieve different goals, among the materials science community. Biosynthesis of metal nanoparticles is easily conducted by several organisms, including plants, bacteria, fungi and algae due to the production of reductant species in many metabolic processes. It is well demonstrated that noble metal ions interact with carboxylates and amino groups at the cell wall, and these anchored ions further reduce developing nanoparticles (Beveridge and Murray, 1980; Klaus et al., 1999; Shedbalkar et al., 2014; Hulkoti and Taranath, 2014; Faramarzi and Sadighi, 2013). Spherical or polyhedral silver or gold nanoparticles have been obtained by several organisms including plants (Iravani, 2011; Narayanan and Sakthivel, 2010; Singh et al., 2015; Gericke and Pinches, 2006), revealing the capacity of living organisms for producing reductant, such as polysaccharides, as well as stabilizing species that inhibit of direct growth in particular directions. Even the mechanism of biosynthesis is not fully understood, there is a wide library of microorganisms producing metallic nanoparticles due to their interesting applications that range from biomedical applications to catalysis, drug delivery and biosensors. Silver nanoparticles are known to exhibit antimicrobial activity (Schröfel et al., 2014; Thomas et al., 2014; Mageswari et al., 2015; Suresh et al., 2010; Okafor et al., 2013), gold nanoparticles are widely used as biosensors (Daniel and Astruc, 2004) and palladium and platinum nanoparticles are used as catalysts in several industrial processes (Cheong et al., 2010; Arenz et al., 2005). The bioreduction of platinum and palladium has been less exploited, even it was demonstrated that Cyanobacteria *Calothrix* and *Leptololyngbya* produce reduction of Pt and Pd by nitrogenases (Brayner et al., 2007), and that algae *Chlorella vulgaris* reduces Pd(IV) by species produced during photosynthesis (Eroglu et al., 2013).

Microorganism-based bioremediation with conversion of toxic heavy metals to nanoparticles is an exciting approach that requires optimization. Biosorption by non-viable biomass is limited for the biosynthesis of oxides and chalcogenides because the metabolism is shut down; even it is not affected by the toxicity of the pollutants present in the effluents. Isolation and selection of heavy metal-resistant microorganisms is a critical issue that can be overcome by selecting strains tolerant to metal pollutants isolated from contaminated soils and waters. Chromosomal or plasmid genes are involved in the mechanisms of metal resistance rendering feasible genetic manipulation for strain improvement (Oger et al., 2003). Once selected, it is essential to determine if the interactions with model metal precursors lead to the formation of the wanted inorganic nanocrystals, and to evaluate that cells maintain a long term removal and nanoparticle biosynthesis ability. This analysis should take into account the optimization of microorganism's growth conditions, such as nutrients, pH, ionic strength and temperature in order to understand the metabolic pathways involved in heavy metal resistance and nanocrystal biosynthesis.

Though the synthesized nanoparticles will be biocompatible for the microorganism producing them, for bioremediation purposes the priority will be to deplete the concentration of toxic cations. Conversion of pollutants into valuable products is an important industrial and environmental challenge. In the particular case of nanoparticles, products require monodispersity and well defined shape, size and crystallinity (Koole et al., 2014). The separation and recovery of nanoparticles is not a minor issue, and for this task it is important to determine whether the nanoparticles were produced inside or outside the cells. Under the stress of being in contact with toxic media, living organisms may exhibit different responses. In an ideal scenario the knowledge of the biosynthesis mechanism will allow a better understanding of the cell functioning and also to know which are the variables that can be tuned to enhance the biosynthesis.

The biosynthesis of metal chalcogenides nanoparticles mediated by microorganisms was less explored than their metallic counterparts; even it can be a useful method for combining detoxification with green chemistry synthesis (Li et al., 2011; Durán and Seabra, 2012;

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