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Biomineralization of tellurium and selenium-tellurium nanoparticles by the white-rot fungus *Phanerochaete chrysosporium*

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ABSTRACT

The release of tellurium (Te) and selenium (Se) oxyanions in the environment poses a strong concern due to their inherent toxicity at high concentrations. *Phanerochaete chrysosporium*, a recognized Se-reducing fungus, was evaluated for its physiological response towards tellurite (TeO_3^{2-}, 10 mg Te L^{-1}) and its mixture with selenite (TeO_3^{2-}+SeO_3^{2-}, 10 mg Te L^{-1}+10 mg Se L^{-1}) in synthetic wastewater in batch conditions (pH 4.5, 30 °C, 150 rpm). Biomineralization of Te and Se by *P. chrysosporium* was also investigated. The response of the fungus towards SeO_3^{2-} (10 mg Se L^{-1}) was used as a reference for understanding its inhibitory effects on TeO_3^{2-} removal. Fungal growth was inhibited in the following order: TeO_3^{2-}+SeO_3^{2-} > SeO_3^{2-} > TeO_3^{2-}. Biomineralization of Te^0 needle-like particles (20–465 nm) and different morphotypes of Se-Te particles (50–600 nm) were ascertained as a result of TeO_3^{2-} and TeO_3^{2-}+SeO_3^{2-} exposure, respectively. The ability of *P. chrysosporium* as a Se- and Te-reducing organism opens up the possibility to exploit this fungus for bioremediation applications and for the biosynthesis of unique nanoparticles.

1. Introduction

Tellurium (Te) is a metalloid that has wide applications in household devices and industrial products due to its thermal, optical and semiconducting properties. Te is extensively used in electronic circuits and devices, rechargeable batteries, thermoelectric materials, cooling devices and solar panels (Turner et al., 2012). The growing interest towards Te is evidenced by the increasing number of review reports on its uniqueness, physicochemical and biological characteristics, and its potential application in the field of environmental biotechnology (Chasteen et al., 2009; Ba et al., 2010; Turner et al., 2012; Chivers and Laitinen, 2015). The potential use of binary Te-compounds has also attracted attention in the last decades. For instance, the development of novel materials such as selenium (Se)-Te composites is promising: such materials offer unique semiconductive and optical properties, as well as enhanced electrical resistance and magnetic resistance properties with potential applications in advanced electronic and optoelectronic devices compared to stand alone Te and Se materials (Sadtler et al., 2013; Sridharan et al., 2013).

Te is scarcely and unevenly distributed in the earth's crust (~1–5 μg kg^{-1}; Belzile and Chen, 2015) and despite technological innovations in the mining industry, extracting Te from natural sources is inherently unsustainable and uneconomical. For elements that are not exploitable under the prevailing economic conditions, the exploration for new sources of these elements or methods to recover them from waste streams (i.e., wastewater) is a preferred choice. Te oxyanions, tellurite (TeO_3^{2-}) and tellurate (TeO_4^{2-}), are present in agricultural and industrial soils (Perkins, 2011), mine tailings and industrial effluents, as well as in natural waters such as rivers and sea water (Biver et al., 2015). The release of these water soluble oxyanions into the environment causes concern owing to the fact that Te is toxic to bacteria even at a concentrations of 1 μg mL^{-1} (Taylor, 1999; Díaz-Vásquez et al., 2015). Of particular concern is the release of TeO_3^{2-}, which is the most toxic Te oxyanion (Chasteen et al., 2009). Ingestion of TeO_3^{2-} has shown to cause peripheral neuropathy in rats and mice

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(Wagner et al., 1995). Although little is known about the Te toxicity in humans, ingestion of TeO_3^{2-} has demonstrated to lead to clinical symptoms such as metallic taste, nausea and vomiting (Yarema and Curry, 2005).

Te and Se, another metalloid whose oxyanions are toxic (Fordyce, 2007), prevail together in wastewater streams; for example in copper and sulfur bearing ores, as well as in effluents from metal processing industries (Soda et al., 2011; Vendruscolo et al., 2017). The treatment of Se and Te containing effluents using biological processes is promising from the perspective of converting the toxic species of Te and Se into their elemental forms (Te^0 and Se^0). These elemental forms are less toxic and more stable than the dissolved species, thus allowing the removal of the metalloids from effluents and potentially recovering unique valuable biocomposites.

The biological removal of the individual metalloids from water, especially for Se has been reported extensively; however, the simultaneous removal of both Se and Te or how the presence of each other affect their removal has been hardly reported in the literature. A number of studies have been reported for the biological removal of Se from different environmental matrices using different biocatalysts (Nacharaiah and Lens, 2015; Turner et al., 2012). Bacteria have been the preferred agent for the biological removal of Se; however, the use of fungi is also promising, particularly for treating mild acidic effluents (pH 3.0–7.0). For instance, *Phanerochaete chrysosporium*, a white-rot fungus, showed Se-reducing abilities, being able not only to remove selenite (SeO_3^{2-}) from mild acidic synthetic water (pH 4.5), but also to synthesize Se^0 nanoparticles in both batch and continuous conditions (Espinosa-Ortiz et al., 2015a, 2015b). Few studies have focused on Te geochemical-microbial cycling in the environment, as well as the removal of Te from polluted effluents. The majority of the research done on this topic has explored the use of bacteria (Taylor, 1999; Chasteen et al., 2009; Ba et al., 2010; Turner et al., 2012), but almost neglecting the potential use of other Te-reducing microorganisms like fungi. The biological co-reduction of Se and Te has been investigated only with halophilic (Kabiri et al., 2009; Motesharrei and Amoozegar, 2014) and heterotrophic aerobic bacteria (Bajaj and Winter, 2014). The simultaneous exposure of microorganisms to Se and Te oxyanions has a unique influence on the microbial ability to reduce and biomineralize these oxyanions (Kabiri et al., 2009; Bajaj and Winter, 2014). The presence of Se, as SeO_3^{2-}, has evidenced to trigger TeO_3^{2-} reduction in heterotrophic aerobic bacteria, thereby accelerating the Te removal rate (Bajaj and Winter, 2014).

This study aims to explore the potential use of *P. chrysosporium* for the treatment of mild acidic effluents containing TeO_3^{2-} as a single pollutant and its combination with SeO_3^{2-} as a pollutant mixture. Fungi have been suggested as potential Se- and Te-reducing organisms capable of synthesizing Se^0 and Te^0, as well as Se and Te methylated compounds (Chasteen and Bentley, 2003; Ba et al., 2010; Espinosa-Ortiz et al., 2015a). This study investigates the response of *P. chrysosporium* upon exposure to TeO_3^{2-} (10 mg Te L^{-1}) and concurrent exposure to TeO_3^{2-} and SeO_3^{2-} (10 mg Te L^{-1}+10 mg Se L^{-1}). The responses of the fungus were envisaged in terms of fungal growth, activity and morphology, as well as the potential of the fungus to biomineralize both Se and Te from synthetic wastewater. Different Se to Te ratios (1:1, 2:1, 4:1 and 1:2) were tested to elucidate the effect of the presence of Se on TeO_3^{2-} reduction. Incubations with SeO_3^{2-} (10 mg Se L^{-1}) were also performed and taken as a point of reference of the response of the fungus towards TeO_3^{2-} induced stress conditions.

2. Materials and methods

2.1. Fungal strain and culturing conditions

The fungal strain *P. chrysosporium* MTCC 787 (Institute of Microbial Technology, Chandigarh, India) was used in this study and grown as described previously (Espinosa-Ortiz et al., 2015a). Briefly, the fungus was cultivated at 37 °C in malt extract agar plates. After 3 days of incubation, the fungal spores were harvested and used to prepare a fungal spore solution. This spore solution was used to prepare several pre-cultivation cultures as required for the experiments (2% *v/v* in 50 mL of liquid medium in 100 mL Erlenmeyer flaks, incubated for 2 days at 30 °C). The flasks were placed in an orbital shaker (Innova 2100, New Brunswick Scientific) set at 150 rpm. The inoculum for the batch experiments consisted of subcultures of the 2 day-old fungus (2% *v/v*, 0.003 g dry biomass L^{-1}). Glucose was used as the sole source of carbon in the synthetic wastewater. In a typical procedure, 10 g of glucose, 2 g of KH_2PO_4, 0.5 g of $MgSO_4 \cdot 7H_2O$, 0.1 g of NH_4Cl, 0.1 g of $CaCl_2 \cdot 2H_2O$, 0.001 g of thiamine, and 5 mL of trace element solution (Tien and Kirk, 1988) were dissolved in 1 L of deionized water and sterilized at 123 kPa and 110 °C for 30 min and cooled at room temperature prior to use. The initial pH was adjusted to 4.5.

2.2. Batch experiments

2.2.1. Exposure to TeO_3^{2-} and TeO_3^{2-} + SeO_3^{2-}

The response of *P. chrysosporium* to the presence of TeO_3^{2-} and its combination with SeO_3^{2-} (TeO_3^{2-}+SeO_3^{2-}) was assessed in batch experiments. *P. chrysosporium* was incubated for 8 days in the presence of K_2TeO_3 (10 mg Te L^{-1}) or combined with Na_2SeO_3 (TeO_3^{2-} + SeO_3^{2-}, 10 mg Se L^{-1} and 10 mg Te L^{-1}). Previously, in batch and continuously operated up-flow bioreactors, it was demonstrated that SeO_3^{2-} has an inhibitory effect on fungal growth and morphology (Espinosa-Ortiz et al., 2015a, 2015b). Hence, in this study, incubations with $NaSeO_3^{2-}$ (10 mg Se L^{-1}) were used as a reference to understand the response of *P. chrysosporium* to TeO_3^{2-} exposure. In all the incubations, glucose was used as the carbon source.

The growth of the fungus and the removal of oxyanions were monitored as a function of incubation time. A total of 21 flasks for each treatment, including controls, were incubated in batch at 30 °C, initial pH 4.5, at 150 rpm and triplicate flasks were sacrificed for the analysis of residual oxyanions and other parameters on days 0, 1, 2, 3, 4, 6 and 8. Biotic controls (untreated) in the absence of any oxyanions as well as abiotic controls (absence of biomass) were also performed to determine the contributions from abiotic reactions.

2.2.2. Reduction of TeO_3^{2-} at different SeO_3^{2-} concentrations

The effect of the SeO_3^{2-} concentration on TeO_3^{2-} reduction was investigated by incubating *P. chrysosporium* with a constant initial TeO_3^{2-} concentration of 10 mg Te L^{-1} and with SeO_3^{2-}concentrations varying between 5 and 40 mg Se L^{-1}. This corresponded to SeO_3^{2-} to TeO_3^{2-} ratios of 1:2, 1:1, 2:1 and 4:1, respectively. The experimental conditions were similar to those described previously in Section 2.2.1. Incubations in this experiment were maintained for 4 days, which was observed (from the time-dependent study described above) to be the period at which most fungal biomass was produced. Batch experiments were conducted in triplicate for each incubation.

2.3. Characterization of fungal morphology

Macro-morphology of the fungal pellets was determined through digital images (Canon EOS Rebel T3, Taiwan). To find out if

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