Bioremoval of arsenic (V) from aqueous solutions by chemically modified fungal biomass

J. F. Cárdenas-González¹ · I. Acosta-Rodríguez¹ · Y. Téran-Figueroa² ·
A. S. Rodríguez-Pérez¹

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Abstract The biosorption of arsenic (V) on nine chemically modified biomasses (with iron oxide coated) of mycelia fungi: *Aspergillus flavus* III, IV and V, *Aspergillus fumigatus* I–II, *Paecilomyces* sp., *Cladosporium* sp., *Mucor* sp-1 and 2 was studied in this work. This study provides evidence that the biomasses of the fungi *A. flavus*, IV, III and V, *Paecilomyces* sp., and *A. fumigatus* I were very efficient at removing 1 mg/L of the metal in solution, using atomic absorption spectroscopy (AAS), achieving the following percentage of removals: 97.1, 92.3, 90.3, 89.0, and 83.4%, respectively. The results of adsorption were obtained at pH 6.0, 30 °C after 24 h of incubation, with 1 g/100 mL of fungal biomass. These results suggest the excellent potential of almost all isolated strains for bioremediation and removal of metals from contaminated sites.

Keywords Biosorption · Arsenic (V) · Fungal biomass · Bioremediation · Heavy metals and metalloids · Environmental pollution

Introduction

Arsenic compounds are very common toxins in the environment, exist in nature contaminating drinking water, arsenic can be found in the earth's crust, ground, marine water and in the organic world as well. It is mobilized through a combination of natural processes such as weathering reactions, biological activity, and volcanic emissions (Biswas et al. 2008; Smedley and Kinniburgh 2002) as well as through a range of anthropogenic activities such as gold mining, non-ferrous smelting, petroleum-refining, combustion of fossil fuel in power plants, and the use of arsenical pesticides and herbicides (Behloul et al. 2016). Arsenic pollution is a well-known environmental problem with severe human health implications, mostly in some countries such as Bangladesh, Vietnam, China, México, and Chile. Chronic exposure to arsenic concentrations above 100 ppb can cause vascular disorders, such as dermal pigments (blackfoot disease) and skin lesions, liver and lung cancer (Desesso et al. 1998; Wang et al. 2001). Other serious diseases such as neurotoxicity, destruction of erythrocytes, hypertension and cardiovascular diseases, DNA damage, and diabetes can be triggered (Dwivedi et al. 2015). World Health Organization (WHO) as a guideline value for drinking water (WHO 1993; Das et al. 2007) has recommended an arsenic concentration of 10 µg/L.

Arsenic is found in soils and natural waters, mainly in the form of arsenate (As (V)) and arsenite (As (III)). The distribution between dissolved As (III) and As (V) is dependent on redox potential and pH. Under oxidizing conditions, the predominant specie is As (V), which exists as deprotonated oxyanion of arsenic acid (H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-}). Under reducing conditions, As (III) is thermodynamically stable and exists in solution as

✉ J. F. Cárdenas-González
jfkardenas_08@hotmail.com

¹ Laboratorio de Micología Experimental, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. Manuel Nava No. 6, Zona Universitaria, 78320 San Luis Potosí, SLP, Mexico

² Laboratorio de Microbiología, Parasitología y Toxicología de Alimentos, Facultad de Enfermería, Universidad Autónoma de San Luis Potosí, Av. Niño Artillero No. 130, Zona Universitaria, 78320 San Luis Potosí, Mexico

arsenious acid, a neutral, uncharged molecule (H_3AsO_3^0) that only forms deprotonated oxyanions at $\text{pH} > 9.2$ ($\text{H}_2\text{AsO}_3^{3-}$ and HAsO_3^{2-}) (Prasad et al. 2013). The As (III) species are more toxic than As (V) and this is electrically neutral and consequently electrostatically is not strongly adsorbed on most mineral surfaces as the negatively charged As (V) oxyanions (Brewster 1992). Due to the exposed characteristics, the arsenic species must be removed because it is a problem of global concern; there are some commonly used techniques for arsenic removal, such as ion exchange, adsorption, chemical precipitation, oxidation–reduction, complexation with metal salts, but these techniques are very expensive and some form more toxic compounds. Currently the use of natural materials and microorganisms are very important, and the iron oxide-coated sand method, which is used to modify the surface of several of these natural biomasses, has a lot of future (Srivastava and Dwivedi 2016).

Iron oxide-coated sand was used in many studies for arsenic removal and the results were positive (Thirunavukkarasu et al. 2003), several studies have been carried out such as modified [iron (III) loaded] orange juice industrial residue (Ghimire et al. 2002), *Penicillium purpurogenum* (Say et al. 2003), arsenate removal by chemicals such as polyelectrolyte, dodecylamine, and cetyl trimethyl ammonium bromide, modified *Penicillium chrysogenum* compared with the unmodified biomass (Luokidou et al. 2003), the biovolatilization of arsenic by *Aspergillus clavatus*, *Aspergillus niger*, *Trichoderma viride*, and *Penicillium glabrum* (Urik et al. 2007), the biological removal of arsenic pollution by *Aspergillus* and *Trichoderma*, *Neocosmospora* sp., *Sordaria* sp., *Rhizopus* sp., *Penicillium* sp., and sterile mycelia strain fungal groups (Srivastava et al. 2011), and the modified fungal biomass of *A. niger* (Pokhrel and Viraraghavan 2006), other important studies mention the substantial changes in the surface with other chemical compounds to prove its potential as biosorbent (Borah et al. 2009). Therefore, with this evidence the aim of this work was to explore the removal of Arsenic (V) in solution by nine modified fungal biomasses.

Materials and methods

Biosorbents and culture conditions

The biosorbents utilized were the fungal biomasses of *Aspergillus flavus* III, IV and V, and *Aspergillus fumigatus* I–II isolated from a mining waste in Zimapán, Hgo, México; *Cladosporium* sp., *Mucor* sp-1 and 2 resistant to zinc, lead, and copper isolated from the air collected near a zinc-smelting plant in San Luis Potosí, S.L.P., México; and *Paecilomyces* sp. isolated from polluted air with industrial

vapors, near of Chemical Science Faculty, located in the city of San Luis Potosí, S.L.P. México. The fungi were grown at 28 °C in agitated and aerated liquid media containing thioglycolate broth (8 g/L). After 4–5 days of incubation, the cells were centrifuged at $700\times g$ for 10 min, washed twice with trideionized water and then dried at 80 °C for 12 h. Finally, the fungal biomass was milled and stored in an amber bottle at a temperature of 4 °C until their use.

Arsenic (V) solutions

For the analysis, a series of solutions with 1 mg/L of arsenic (V) ($\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$, Sigma Chemical Co., USA) were prepared, pH was adjusted with nitric acid and/or NaOH, and the quantity of biomass added to each flask was of 1 g/100 mL for the arsenic solution. Samples were taken at different times, the biomass was removed by centrifugation at $700\times g$ during 10 min and the concentration of the metal ions was determined in the supernatant.

Preparation of iron oxide-coated biomasses

80 mL of 2 M $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was prepared and 1.0 mL of 10 M NaOH was added to this solution and mixed thoroughly. 20 g of the fungal biomass powder was taken in a porcelain pot, a mixture of iron oxide and NaOH solution was added to the porcelain pot and homogenized and kept at 80 °C for 3 h. Afterward, the temperature was raised to 110 °C and stayed there for 24 h. The coated biomass powder was separated by crushing with mortar and pestle (Pokhrel and Viraraghavan 2006).

Determination of arsenic (V)

The concentration of arsenic ions in solution was determined by atomic absorption spectroscopy (AAS) (Atomic Absorption Spectrometer Varian, Model Spectra A-20). All experiments were carried out in triplicate and the results were presented as mean $\pm$ standard deviation.

Results and discussion

Arsenic removal by native and iron oxide-coated biomass at different pH

Figure 1 shows the effect of native and iron-coated biomass, also pH, on biosorption of As (V) ions (1 mg/L, 24 h). It was found that the removal is minor in unmodified biomass, in comparison with the modified biomass, because at 24 h of incubation and pH 6.0, there was a 10.1% (0.101 mg/L) of removal (Fig. 1), and these results

Fig. 1 As (V) removal by native and iron-coated biomass at different pH. 1 mg/L As (V), 30 °C, 100 rpm, 1 g of fungal biomass of *Paecilomyces* sp.

are better than those reported for *A. clavatus*, *A. niger*, *T. viride*, and *P. glabrum* (Urik et al. 2007), with removal between 0.010 and 0.067 µg/L, and are lower than those reported for *P. purpurogenum*, 3.4 mg/g of biomass (Say et al. 2003). Structural properties of the biosorbent including the cellular support and other several factors are known to affect the biosorption rate (Bayramoglu et al. 2003). With respect to the iron-coated biomass, the removal of As (V) was very efficient (89%, pH 6.0, 24 h) (Fig. 1), this could be because the dominant species in this pH is H_2AsO_4^- , which likely forms a complex with iron-coated biomass. At a higher pH, OH^- ions in the solution increase, which compete with arsenate ions and, therefore, the adsorption of As (V) is reduced (Raje and Swain 2002). Considering that there was no other chemical reaction between the iron oxide and the biomass, the mechanism of As (V) removal could be similar to arsenic adsorption on iron oxide-coated sand (Thirunavukkarasu et al. 2003). These results are similar to those described in other reports: by iron (III)–poly(hydroxamic acid) complex (Haron et al. 1999), iron oxide-coated sand (Thirunavukkarasu et al. 2003), chemically modified fungal biomass (Luokidou et al. 2003), iron oxide-coated biomass of *A. niger* (Pokhrel and Viraraghavan 2006), mixed metal oxide impregnated with chitosan beads (Yamani et al. 2012), and by iron-modified activated carbon (Chen et al. 2007).

The effect of incubation time on As (V) removal

The biosorption of 1 mg/L of As (V) onto iron-coated biomass with different time interval (0–24 h) at pH 6.0 and 1 g/L of biosorbent material is shown in Fig. 2. The biosorption study of As (V) ions as function of contact time (incubation time) showed that the best results are given at 24 h, which indicates availability of the biosorption sites. The kinetics of sorbent metal interaction at optimum pH may be acknowledged to enhance accessibility of the chelating sites of the biosorbent material (Raje and Swain

Fig. 2 Effect of the incubation time on the removal of 1 mg/L of As (V). 30 °C, 100 rpm, pH 6.0, 1 g of iron-coated fungal biomass of *Paecilomyces* sp.

2002). With further increase in time, no significant enhancement was observed in removal of As (V). These results were similar for iron modified with activated carbon, with a removal of 1 mg/100 mL at 24 h (Chen et al. 2007), and were different from the other reports, iron oxide-coated biomass of *A. niger* (80.1 mg/L, 12 h) (Pokhrel and Viraraghavan 2006).

Effect of the temperature on As (V) removal

Figure 3 shows the effect of varying temperatures (30, 37, 42, and 50 °C). The maximal adsorption capacity was found at 30 ± 1 °C (89%) and the adsorption capacity of the iron-coated biomass of *Paecilomyces* sp. decreased with temperatures higher than 30 ± 1 °C (83% at 37 °C, 79% at 42 °C, and 76%, at 50 °C). This is different from the report for iron oxide-coated biomass of *A. niger* (Pokhrel and Viraraghavan 2006). The temperature of the adsorption medium could be important for energy-dependent mechanisms in metal biosorption by microorganisms. Energy-independent mechanisms are less likely to be affected by temperature since the process responsible for biosorption is largely physicochemical in nature (Pokhrel

Fig. 3 Effect of the temperature on the removal of 1 mg/L of As (V). 100 rpm, pH 6.0, 1 g of iron-coated fungal biomass of *Paecilomyces* sp.

and Viraraghavan 2006). The biosorption of As (V) by *Paecilomyces* sp. fungus appears to be temperature dependent over the temperature range tested (30–50 °C).

Effect of initial As (V) concentration

Biosorption capacities of the iron-coated biomass of *Paecilomyces* sp. for the As (V) ions were studied as a function of the initial As (V) ions concentration between 1 and 5 mg/L in the biosorption medium (Fig. 4), and we observed that the percentage of adsorption decreased, when ions concentration increased. A similar trend was reported for the removal of Hg(II) from aqueous solution by sorption on *R. oligosporus* (Ozsoy 2010). These results may be explained due to the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the biomass at higher concentrations (Baig et al. 2010).

Effect of initial biomass concentration

The influence of the modified biomass on the removal capacity of As (V) is depicted in Fig. 5. If we increase the amount of *Paecilomyces* sp. biomass, the removal of the metal in solution also increases (99.3% with 5 g of fungal biomass, at 24 h), with more biosorption sites of the same, because the amount of added biosorbent determines the number of binding sites available for metal biosorption (Huang 2014; Singh et al. 2014). Similar results have been reported for iron-modified activated carbon (Chen et al. 2007), with a removal of 80%, respectively.

Application on natural water

This study showed the potential of iron-coated fungal biomass for the removal of As (V) at different conditions. The main advantage of this biosorbent material is their ability to growth easily with low cost. The biosorbent

Fig. 4 Effect of the concentration of As (V) in solution on the removal of As (V) ions. 100 rpm, 30 °C, pH 6.0, 1 g of iron-coated fungal biomass of *Paecilomyces* sp.

Fig. 5 Effect of fungal biomass concentration on the removal of 1 mg/L of As (V). 100 rpm, 30 °C, pH 6.0

material was successfully used for the removal of As (V) from water samples of sediments having 1 mg/L (adjusted) from Cerrito Blanco, Matehuala, San Luis Potosí, and México. The water sample studied is highly contaminated with As (200,000 µM) due to a contamination of the subterranean water by mining activities (Torres and Martínez 2010), which indicated that it was out of the maximum allowable limit for drinking water (0.05 mg/L), according to NOM-127-SSA1-1994. Currently it is 0.025 mg/L, according to NOM-127-SSA1-1994-2000 (1994) and NOM 014-SSA1 (1993), respectively. It may be seen that after biosorption of As (V), this was reduced to a value of 0.220 mg/L, with 0.78 mg/L of removal of As (V) in natural water contaminated with 1.0 mg/L of As (V) under the following characteristics, 5 g of iron-coated biomass, 100 rpm, 30 °C, pH 6.0, and 24 h of incubation, showing the efficiency of biosorbent material for the removal of As (V) ions from pole water samples, and the results were similar for arsenical removal with ion-exchange resins (Prieto et al. 2012).

Biosorption of arsenic (V) by different iron-coated fungal biomass

Figure 6 shows the biosorption of arsenic (V) by the different biomasses analyzed. It was found that the modified biomass of the fungi *A. flavus* IV, III, V, and *Paecilomyces* sp. were very efficient at removing the metal in solution (97.1, 92.3, 90.3, and 89%, respectively). We do not know why the fungal biomasses of *A. flavus* were the most efficient at removing arsenic (V) in solution. However, that difference may be because the polysaccharides of the cell wall could provide binding groups including amino and carboxyl groups, and the nitrogen and oxygen of the peptide bonds could be accompanied by displacement of protons, dependent in part upon the extent of protonation as determined by the pH (Bartnicki-García 1968), and some of this fungal biomass can remove mercury (II) in solution (Martínez et al. 2012).

Fig. 6 Biosorption of 1 mg/L of As (V) on different iron-coated biomasses. 100 rpm, 30 °C, pH 6.0, 1 g of modified fungal biomass

Conclusion

In this study, As (V) uptake by iron-coated fungal biomasses was studied. The performance of the biosorbents was examined as a function of the operating conditions, in particular, incubation time, pH, initial metalloid ion concentration, and fungal biomass. The experimental evidence showed a strong effect of the experimental conditions. Modification on biomass surface leads to increase in the biosorption which showed that the modified iron oxide-coated biomass increases the removal of As (V) ions from aqueous solution, unlike native biomass. When the ease of production and economical parameters are concerned, it was observed that the fungi analyzed are a very promising biomaterial for removal or recovery of the metal ion studied.

Compliance with ethical standards

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