The complexity of biosorption treatments for oxyanions in a multielement mine effluent

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Abstract

Selenium (Se) is a contaminant in effluents from coal mines and coal-fired power stations, where it is encountered as the oxyanion selenate (SeO_4^{2-}, hereafter SeVI). SeVI can be removed from solution with Fe-treated biosorbents, but the efficacy of these treatments in effluents with multiple contaminants is unclear. This study investigates the interactions between SeVI and the oxyanions SO_4^{2-} and NO_3^-.

1. Introduction

Biosorption of contaminants from industrial effluents using dried algal biomass is a promising approach to the sustainable treatment of industrial effluents (Gadd, 2009). However, one limitation to the use of algal biomass as a biosorbent is that dried algae are only effective at adsorbing a sub-set of the many elements that are common in industrial effluents (Kidgell et al., 2014). One critical metalloid often found in effluents from coal mining and processing facilities is the oxyanion selenate (SeVI) (Chapman et al., 2009). SeVI is toxic at concentrations slightly in excess of essentiality due to its tendency to impair the function of enzymes in vertebrates (Hamilton, 2004; Yang et al., 2010). SeVI, like most metalloids, is difficult to remove from effluents as it is encountered as an oxyanion (Sappington, 2002; Mondal et al., 2004) for which passive biosorbents have a low affinity (Mondal et al., 2004; Ghazvini and Mashkani, 2009; Figueiredo and Quintelas, 2014). However, algal-based biosorbents can be modified by a treatment of ferric chloride (FeCl_3) followed by pyrolysis to yield an Fe-treated biochar with a high biosorption capacity for SeVI in solution (Roberts et al., 2014).

One potentially abundant source of biomass for biosorption applications is the use of the waste biomass produced in the commercial extraction of agar from cultivated red seaweeds. The main genus of algae grown for the extraction of agar is Gracilaria. Commercial cultivation of Gracilaria is increasing rapidly worldwide, particularly in Indonesia where more than 500,000 tonnes are produced annually (Sibeni and Calderini, 2012). The granular material remaining after the extraction of agar is currently stored as a waste with no economic value or further use (Seo et al., 2010). However, Roberts et al. (2014) demonstrated that the waste can be used to produce a biosorbent with a high capacity to adsorb SeVI by treating the Gracilaria extraction waste with FeCl_3. The biosorbent had high removal rates of Se, both as selenite (SeIV) and SeVI, within the course of a few hours. Furthermore, the biosorption capacity was increased 3-fold once the FeCl_3-loaded biomass was converted into biochar through pyrolysis. Biosorption of SeVI by the final product, Gracilaria Modified Biochar (GMB), was pH and temperature independent, negating the need to adjust both the...
pH and the temperature prior to biosorption of any industrial effluent and significantly simplifying the method (Roberts et al. 2014).

However, one limitation of this biosorption process, and of analogous processes, is that it is typically not assessed using real-world effluents. Rather, research has focused on the biosorption of elements from simple mock solutions with single elements (Gadd, 2009). The behavior of a biosorbent in real-world effluents, such as mine effluents, is much more complex than the behavior in mock solutions (Kidgell et al. 2014). The advantage of examining biosorption capacities using real-world effluents is that it offers insight into potential interactions among elements (Vijayaraghavan and Joshi, 2013) and specifically the differences between metals and metalloids (Kidgell et al. 2014). The presence of non-target elements with similar properties may impede the uptake of the target element due to competition for common uptake sites (Brix et al. 2001; Hamilton, 2004).

Sulfate (SO4\(^{2-}\)) is a common oxyanion in effluent waters from coal mines, particularly in areas where coal has a high S content (Rodriguez et al. 2012). SO4\(^{2-}\) is known to interfere with the bioremediation of SeVI by passive biosorbents (Lalvani, 2004; Yamani et al. 2014). For example, the bioremediation of SeVI in effluent waters is reduced in the presence of SO4\(^{2-}\), irrespective of the type of biosorbent used (Lalvani, 2004; Yamani et al. 2014). Alumina, chitin, activated carbon and impregnated chitosan beads all have a reduced capacity for the biosorption of SeVI in the presence of SO4\(^{2-}\) (Lalvani, 2004; Dobrowolski and Otto, 2012; Yamani et al. 2014). Nitrate (NO3\(^{-}\)) is another common constituent of mining effluents, especially in effluents where ammonium nitrate and fuel oil (ANFO) explosives are used on site, which can interfere with the biosorption of SeVI. For example, the biosorption of SeVI from agricultural drain water, using soil as a biosorbent, was reduced when the concentrations of NO3\(^{-}\) was 5 mg L\(^{-1}\) or more (Bailey et al. 2012). While it is clear that the presence of other oxyanions interferes with the uptake of SeVI by a biosorbent (Lalvani, 2004; Bailey et al. 2012; Dobrowolski and Otto, 2012; Yamani et al. 2014), it is uncertain whether the iron-based biosorbents have an affinity for other oxyanions that interfere with the uptake of SeVI. Answering this question will require experiments that first examine the biosorption capacity of an iron-based biosorbent to oxyanions in mock solutions and then examine the biosorption capacity of the iron-based biosorbent in a complex real-world effluent with multiple oxyanions.

This study examines the comparative ability of GMB to remove SeVI from a single-element mock solution and a mine effluent that is contaminated with the potentially inhibiting oxyanions SO4\(^{2-}\) and NO3\(^{-}\). The specific aims of this paper are to 1) compare the biosorption capacity of GMB for SeVI in both a single-element mock solution and in a real-world mine effluent, 2) compare the biosorption capacity of GMB for target (SeVI) and non-target (SO4\(^{2-}\) and NO3\(^{-}\)) constituents of mock solutions, and 3) determine the biosorption capacity of the GMB for SeVI as a function of differing relative concentrations of non-target (SO4\(^{2-}\) and NO3\(^{-}\)) compounds to quantify the interactions between elements. This information will establish the performance of the biosorbent under real-world mine conditions as a step towards understanding the industrial application of a promising SeVI treatment.

2. Materials and methods

2.1. Real-world mine effluent

A sample of a mine effluent was obtained from a coal mine operated by Anglo American Coal (Canada). The sample was collected in June 2013 from an effluent sedimentation pond and cold-shipped to James Cook University in Townsville, Australia. The effluent was stored in a fridge at 4 °C until use. The concentration of total Se was 108 μg L\(^{-1}\) and speciation analyses showed this to be 99% SeVI with a small amount of SeIV. The elemental composition of the effluent is shown in Table S1.

2.2. Biomass preparation

Gracilaria extraction waste was obtained from AgarIndo Bogatama in Indonesia (for details see Roberts et al. 2014). Prior to use as a biosorbent, the Gracilaria extraction waste was rinsed with MilliQ water and dried in an oven at 60 °C for 24 h. The dry biomass was then loaded with a 5% FeCl3 solution (Sigma Aldrich) at a rate of 25 g biomass L\(^{-1}\) for 24 h at 15 °C before being rinsed twice with MilliQ water to remove excess FeCl3. After a second drying in the oven at 60 °C for 24 h, the FeCl3-loaded biomass was converted into GMB by a pyrolysis process where the biomass was pyrolysed at a temperature of 450 °C for 1 h while being continuously purged with N2 gas at a rate of 4 L min\(^{-1}\) (Bird et al. 2011). The biochar was then cooled to room temperature under continuous N2 flow and stored for use.

2.3. Performance of GMB in SeVI mock solution and mine effluent

A biosorption experiment was performed to compare the performance of GMB in a SeVI mock solution and a real-world mine effluent containing SeVI and the oxyanions NO3\(^{-}\) and SO4\(^{2-}\). The concentration of SeVI in the mock solution was prepared to reflect that in the effluent (108 μg L\(^{-1}\)) at 100 μg L\(^{-1}\). Total Se was measured to allow a direct comparison of performance in the two solutions. Since both solutions contained 99% SeVI, data for total Se are hereafter referred to as SeVI.

A 1 g L\(^{-1}\) SeVI solution was made by mixing Na2SeO4 (Sigma Aldrich) with MilliQ water after which the solution was diluted to 100 μg L\(^{-1}\). The mock solution and the mine effluent were treated multiple times with GMB to measure sequential reductions in dissolved SeVI after multiple deployments of biosorbents. Each treatment involved exposing the SeVI source (mock or effluent) to a number of deployments of new GMB (1, 2, 3, 4, 6, 8, 10, 12 or 14 sequential deployments). Each replicate consisted of a 250 ml container containing 1 g GMB and 100 ml of mock SeVI solution or mine effluent. The GMB was exposed to the mock SeVI solution or effluent for 1 h at 15 °C in a shaker incubation cabinet (100 rpm). After 1 h the solution was filtered using a 75 μm filter mesh and transferred into a new container with 1 g of new GMB. The final solution for each treatment was collected for analysis of total Se after the final deployment. The solution was filtered out from the GMB as described above, after which it was filtered with a 0.45 μm syringe filter and collected in falcon tubes. Stock solutions were sampled at the start of the experiment to determine initial starting concentrations.

2.4. Comparative assessment of the biosorption capacity of GMB for SeVI, SO4\(^{2-}\), and NO3\(^{-}\)

A biosorption experiment was conducted to evaluate the relative biosorption capacity of the GMB for the target SeVI and non-target compounds SO4\(^{2-}\) and NO3\(^{-}\) in equimolar solutions. Biosorption capacity, in this study, is defined as q, with a higher q signifying a higher biosorption capacity of the GMB to an oxyanion and the highest biosorption capacity referred to as q\(_{\text{max}}\). q is expressed as the amount of an element removed per gram biosorbent (e.g. 1.2 μg SeVI g\(^{-1}\) GMB).

To identify the biosorption capacity of GMB for each of the compounds, a q\(_{\text{max}}\) kinetic experiment was undertaken. Seven concentrations of SeVI, SO4\(^{2-}\) and NO3\(^{-}\) were prepared (0.01, 0.05, 0.1,
0.5, 1, 1.5 and 5 mM) in MilliQ water from three stock solutions (Na2SeO4, Na2SO4 and NaN3, respectively) (Sigma Aldrich). The concentrations were selected to encompass the equilibrium concentration that delivers a SeVI qmax value for the GMB (Roberts et al. 2014). To run the experiment, 0.3 g of GMB was first weighed out into 250 ml acid washed plastic containers and then exposed to 30 ml of one of the solutions for 1 h at 15 °C and 100 rpm. The biomass was filtered out directly following the exposure using a 75 μm filter mesh and collected in falcgon tubes and dried in a drying oven at 60 °C. The solution was filtered using a 0.45 μm syringe filter and collected in falgon tubes before being analysed. Samples of the seven stock solutions were taken at the start of the experiment to determine initial starting concentrations. The q value at each point was calculated according to the equation (Volesky, 2007): (1)

\[ q = \left( \frac{W_i - W_f}{M} \right) \times V \]

where, \( W_i \) is the initial concentration (mg L\(^{-1}\)) of SeVI, SO4\(^{-2}\) and NO3\(^{-}\), \( W_f \) is the final concentration (mg L\(^{-1}\)) of SeVI, SO4\(^{-2}\) and NO3\(^{-}\), V is the volume (in L) of water used in the experiment, and M is the mass of biochar (g) used in the experiment.

2.5. The effect of SO4\(^{-2}\) and NO3\(^{-}\) on SeVI biosorption

An experiment was conducted to examine the effects of the non-target compounds SO4\(^{-2}\) and NO3\(^{-}\) on the uptake of SeVI by GMB. To do this, the GMB was exposed to 100 μg L\(^{-1}\) SeVI in the presence of non-target compounds (SO4\(^{-2}\) and NO3\(^{-}\)) at different molar ratios. The concentration of SeVI was prepared to match the concentration of SeVI in the mine effluent so that the capacity of the biosorbent could be evaluated under realistic conditions. The molar ratios of SeVI:SO4\(^{-2}\) and SeVI:NO3\(^{-}\) were determined to include the existing ratios of these compounds in the mine effluent as described below.

The mine effluent contained 643 mg L\(^{-1}\) SO4\(^{-2}\) (6.7 mM L\(^{-1}\)) and 158 mg L\(^{-1}\) NO3\(^{-}\) (2.5 mM L\(^{-1}\)). With a concentration of 108 μg L\(^{-1}\) SeVI (0.0007 mM L\(^{-1}\)), the effluent had a SeVI:SO4\(^{-2}\) ratio of approximately 1:9500 and a SeVI:NO3\(^{-}\) ratio of approximately 1:3600. The biosorption of SeVI was therefore investigated at molar ratios of 1:0 (SeVI only as a control) and 1:0.5, 1:1, 1:10, 1:100 and 1:10,000. With an initial SeVI concentration of 0.0007 mM L\(^{-1}\), the molar concentrations of SeVI:SO4\(^{-2}\) and SeVI:NO3\(^{-}\) in the treatments were 0.0007:0, 0.0007:0.000035, 0.0007:0.0007, 0.0007:0.0007, 0.0007:0.0007, 0.0007:0.0007, 0.0007:0.0007 and 0.0007:7.7 mM.

A 100 mM stock solution was prepared for SO4\(^{-2}\) and NO3\(^{-}\) by dissolving Na2SO4 and NaN3 (Sigma Aldrich) in MilliQ water. The SO4\(^{-2}\) and NO3\(^{-}\) stock solutions were then diluted with MilliQ water to give 1 L of each of the 7 concentrations. The SeVI was then added to each solution by pipetting in 100 μL of a 1 g L\(^{-1}\) SeVI stock solution (made from Na2SeO4 Sigma Aldrich). Three replicates of each molar ratio were run by adding GMB to an aliquot of the solution (10 g L\(^{-1}\)) and placing it on a shaker plate (1 h at 15 °C and 100 rpm). After one hour the solution was filtered (0.45 μm syringe filter) and analysed according to the previously described methods. Stock solutions were taken at the start of the experiment to determine initial starting concentrations. The removal of SeVI was calculated as the difference between initial and final concentrations for each treatment.

2.6. Elemental analysis

Analysis of SeVI was carried out by the Advanced Analytical Centre at James Cook University using a Varian 820-MS Inductively Coupled Plasma Mass Spectrometer (Melbourne, Australia) with a detection limit of 1 μg L\(^{-1}\). The isotope 82Se was used for the quantification of SeVI as other isotopes of SeVI were interfered with by ClAr\(^{+}\) or ArAr\(^{+}\). External calibration used a series of SeVI standard solutions where indium was used as the internal standard to correct for instrument drift and potential matrix effects. A 1% HCl solution was spiked with 1 ppb SeVI and measured three times for quality control. A recovery of between 98.5 and 110% showed no significant interferences. Procedural controls without GMB showed no change over the experimental period indicating no measurable loss of SeVI to experimental plastic ware. SO4\(^{-2}\) and NO3\(^{-}\) were analysed by TropWater at James Cook University, using an OI Analytical Flow IV Segmented Flow Analyzer and a Thermo Scientific Gallery Discrete Analyzer. SO4\(^{-2}\) was analysed with the standard method 4500-SO4 \(– E\) and NO3\(^{-}\) was analysed with the APHA standard method 4500-NO3 \(F\) method (Eaton et al. 2005) with detection limits of 1 mg L\(^{-1}\) for both SO4\(^{-2}\) and NO3\(^{-}\).

2.7. Statistical analysis

To examine the adsorption capacity of the GMB for SeVI, SO4\(^{-2}\) and NO3\(^{-}\) over multiple deployments, one-way ANOVAs were run for each oxyanion separately using square-root transformed data to meet the assumptions for normality and homogeneity of variance. Tukey's Post Hoc test was used to detect differences between exposure times.

The affinity of GMB for SeVI, SO4\(^{-2}\) and NO3\(^{-}\) was analysed separately for each oxyanion. The percent uptake from initial to final concentration in each replicate, and the means of each exposure time, were analysed separately by one-way ANOVA. Data were square-root transformed to meet the assumptions for normality and homogeneity of variances after which Tukey's post hoc test was used to detect differences between exposure times. q was expressed as the amount of an element removed per gram biosorbent for each element at 7 different concentrations, where qmax was the amount of each element per gram biosorbent at the highest concentration tested. A line of best fit (logarithmic) was fitted to the data to characterise the trajectory of GMB saturation.

The biosorption of SeVI as a function of the oxyanions SO4\(^{-2}\) and NO3\(^{-}\) by the GMB was analysed as percent uptake from initial to final concentration for SeVI in each replicate and the means of each exposure time was analysed by one-way ANOVA. Tukey's post hoc test was used to detect differences between elemental ratio treatments. All data were checked for homogeneity of variances and no transformation was needed. Data were plotted as percent SeVI uptake at 7 ratios of SeVI to SO4\(^{-2}\) and NO3\(^{-}\) and a line of best fit was fitted to the data (exponential).

3. Results

3.1. Performance of GMB in SeVI mock solution and mine effluent

The vast majority of SeVI in the mock solution was adsorbed by the GMB within minutes of exposure to the biosorbent. After the first deployment of GMB into the mock solution, 98% of the SeVI was removed, significantly reducing the concentration of SeVI from 100 to 1.6 μg L\(^{-1}\) (ANOVA: F\(_{20}\) = 2094.11, P < 0.001) (Fig. 1a).

In contrast to the rapid removal of SeVI from the mock solution, a single deployment of GMB in the real-world mine effluent removed only 3% of the SeVI from the effluent (Fig. 1b). At the same time, the first deployment of GMB removed 4% of SO4\(^{-2}\) and 24% of NO3\(^{-}\) (Fig. 1c and d). Given the difference in the initial concentrations of the three elements, this equated to q values of 0.31 μg SeVI removed g\(^{-1}\) GMB, 3.27 mg SO4\(^{-2}\) g\(^{-1}\) GMB and 5.01 mg NO3\(^{-}\) g\(^{-1}\) GMB. After the second deployment, concentrations in the mine effluent had
been reduced by 12% for SeVI, 7% for SO$_4^{2-}$ and 33% for NO$_3^-$ in the last deployment (14 sequential exposures to unused GMB) the concentrations of SeVI, SO$_4^{2-}$ and NO$_3^-$ in the real-world mine effluent had reduced by 63, 27 and 85%, respectively (Fig. 1b, c and d). This equated to a cumulative removal of each of the oxyanions from the effluent of 7 mg SeVI, 21.7 mg SO$_4^{2-}$ and 17.6 mg NO$_3^-$ (Fig. 2). A minimum of 4 deployments were required for SeVI to show a significant difference to the initial SeVI concentration of 108 mg L$^{-1}$ (ANOVA: $F_{9, 19} = 50.15$, $P < 0.001$ and Tukey’s HSD: $P = 0.002$). A significant reduction in SO$_4^{2-}$ was noted between all deployments and the initial concentration of 643 mg L$^{-1}$ SO$_4^{2-}$, with the exception of the first deployment (ANOVA: $F_{9, 19} = 110.06$, $P < 0.001$). Furthermore, the concentration of NO$_3^-$ in all deployments were significantly less than the initial concentration of 158 mg L$^{-1}$ NO$_3^-$ and showed a slight decrease in the rate of uptake after 8 deployments (ANOVA: $F_{9, 19} = 591.08$, $P < 0.001$).

3.2. Comparative assessment of the biosorption capacity of GMB for SeVI, SO$_4^{2-}$ and NO$_3^-$

There was a considerable difference in the biosorption capacity of the GMB for SeVI, SO$_4^{2-}$ and NO$_3^-$ in equimolar mock solutions. The GMB had a $q_{max}$ of 0.03 mM g$^{-1}$ for SeVI, 0.01 for SO$_4^{2-}$ and 0.04 for NO$_3^-$ (3.80, 1.23 and 2.55 mg g$^{-1}$, respectively) (Fig. 3). Overall, GMB had the highest biosorption capacity for NO$_3^-$ followed by SeVI and SO$_4^{2-}$. Somewhat surprisingly, at low initial concentrations (0.05 and 0.1 mM) GMB had a higher $q$ value for SO$_4^{2-}$ demonstrating that the relationship is non-linear and a function of initial concentrations (Table S2). The response was non-linear for all three elements.

The lower concentrations of SeVI, SO$_4^{2-}$ and NO$_3^-$ showed the highest percent change between initial and final concentrations. However, the biosorption capacity of the GMB was greatest at the highest concentrations (Fig. 3). The greatest percent removal of SeVI was 99% at both the 0.01 and 0.05 mM concentrations. The highest removal of SO$_4^{2-}$ was at 93% at 0.05 mM and at 43% at 0.5 mM for NO$_3^-$. The removal of SeVI at both 0.01 and 0.05 mM was significantly different to the other concentrations tested (ANOVA: $F_{6, 14} = 418.31$, $P < 0.001$). There was significant differences in the uptake of SO$_4^{2-}$ between the concentrations at which the highest (0.05 mM) and lowest (5 mM) uptake was detected (ANOVA: $F_{6, 14} = 302.60$, $P < 0.001$). The removal of NO$_3^-$ was relatively consistent across concentrations and only the 0.01 and 0.05 mM concentrations were significantly different to the percent uptake at 5 mM (ANOVA: $F_{6, 14} = 4.51$, $P = 0.010$). The line of best fit was a logarithmic relationship between the concentration of elements in solution and on the GMB with $R^2$ values of 0.83 for SeVI, 0.84 for SO$_4^{2-}$ and 0.91 for NO$_3^-$. 

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Fig. 1. Concentrations of SeVI (mg L$^{-1}$ ± SE) in (a) mock solution and (b) a real-world mine effluent, and concentrations of (mg L$^{-1}$ ± SE) of the competing oxyanions (c) SO$_4^{2-}$ and (d) NO$_3^-$ in a real-world mine effluent after multiple exposures to GMB. Overall maximum percent removal for each oxyanion can be found in the top right corners of each panel.

Fig. 2. Cumulative mass (mg) of SeVI (▲), SO$_4^{2-}$ (■) and NO$_3^-$ (●) removed from solution by GMB after multiple exposures.
3.3. The effect of $\text{SO}_4\text{^2-}$ and $\text{NO}_3\text{^-}$ on $\text{Se}^{\text{VI}}$ biosorption

The biosorption capacity of GMB for $\text{Se}^{\text{VI}}$ was affected by increasing levels of $\text{SO}_4\text{^2-}$, but not by the presence of $\text{NO}_3\text{^-}$, across the molar ratios tested in this experiment (Fig. 4a and b). The GMB removed 93% of $\text{Se}^{\text{VI}}$ from solution in the absence of non-target compounds. The biosorption of $\text{Se}^{\text{VI}}$ was reduced by 2%–91% when the concentration of $\text{SO}_4\text{^2-}$ was less than the concentration of $\text{Se}^{\text{VI}}$ (i.e. at molar ratios of 1:0.5) (Fig. 4a). There was a further decrease in the biosorption of $\text{Se}^{\text{VI}}$ to 83%–89% when $\text{Se}^{\text{VI}}$: $\text{SO}_4\text{^2-}$ concentrations were 1:1 or 1:10. At molar ratios 1:100, 65% of the $\text{Se}^{\text{VI}}$ was removed compared to a <10% removal of $\text{Se}^{\text{VI}}$ at molar ratios of 1:1000. No removal of $\text{Se}^{\text{VI}}$ from the solution was detected at the molar ratio representing that of the mine effluent, 1:10,000.

The relationship between the biosorption of $\text{Se}^{\text{VI}}$ and the molar ratio of $\text{Se}^{\text{VI}}$: $\text{SO}_4\text{^2-}$ was well described by the Equation (2):

$$y = 85.7623 \cdot e^{-0.0027x}$$

where $y$ is the percent removal of $\text{Se}^{\text{VI}}$ from a 100 µg L$^{-1}$ solution and $x$ is the molar ratio of $\text{Se}^{\text{VI}}$: $\text{SO}_4\text{^2-}$.

There was no effect of $\text{NO}_3\text{^-}$ on the removal of $\text{Se}^{\text{VI}}$ from solution at molar ratios up to and exceeding those revealed in the effluent. The GMB removed >90% $\text{Se}^{\text{VI}}$ from the $\text{Se}^{\text{VI}}$: $\text{NO}_3\text{^-}$ solution in all treatments tested (Fig. 4b) which was surprising considering the relatively high affinity of GMB for $\text{NO}_3\text{^-}$ (Figs. 3 and 4b).

4. Discussion

Algal-based biosorption has long been proposed as a sustainable and cost-effective means of treating industrial effluents, however, there has been little application of the approach at scale (Voletsky, 2001; Gadd, 2009; Vijayaraghavan and Joshi, 2013). There are two possible explanations for this limited application. Firstly, biosorption is rarely empirically tested in real-world effluents (but see Kidgell et al., 2014) and so there are uncertainties regarding the true potential to treat complex effluents with biosorbents. Secondly, biosorbents typically display limited selectivity for target elements in multi-element solutions. Examining the efficacy of algae for the biosorption of contaminants in real-world industrial effluents is therefore essential to understand how biosorption will occur in complex multi-element sources as a precursor to developing commercial strategies to make this process economically viable.

In this study, GMB had an almost 100% immediate effectiveness in mock $\text{Se}^{\text{VI}}$ solutions that contained concentrations of $\text{Se}^{\text{VI}}$ typical of coal-mining operations (108 µg L$^{-1}$). However, in the real-world mine effluent with the same initial concentration of $\text{Se}^{\text{VI}}$, the biosorption of $\text{Se}^{\text{VI}}$ was significantly impeded by the presence of high concentrations of $\text{SO}_4\text{^2-}$. To improve the biosorption of $\text{Se}^{\text{VI}}$ from the mine effluent it is critical to reduce the concentration of $\text{SO}_4\text{^2-}$. Our data show that the critical $\text{Se}^{\text{VI}}$: $\text{SO}_4\text{^2-}$ molar ratio, that can deliver...
considerable biosorption, is 1:10. Therefore, we predict that the GMB will only be effective at removing 89% of the available SeVI when the SO4^2- concentration is < 0.67 mg L\(^{-1}\) in the mine effluent. Currently, the concentration of SO4^2- in the effluent is approximately 640 mg L\(^{-1}\) meaning that a reduction of 99.9% of the current SO4^2- concentration is required for GMB to reduce the concentration of SeVI in the effluent by any considerable amount.

GMB can be used as an efficient biosorbent to reduce concentrations of SeVI with 85% in mine effluents if the molar concentration of SO4^2- is 10-fold that of SeVI. Interferences by SO4^2- on the removal of SeVI are not uncommon. Yamani et al. (2014) recorded a lack of competition between SeVI and NO3^− for biosorption of SeVI using impregnated chitosan beads as a biosorbent in agricultural drain water. They found that the biosorbent removed 80% of the available SeVI in the absence of SO4^2- compared to only 10% when the concentration of SO4^2- was 10-fold that of SeVI. Interestingly, they also noticed that at low levels (1:0.1) SO4^2- had a minor impact on the uptake of SeVI by the biosorbent.

To combat the effects of the interacting oxyanion SO4^2- on the biosorption of SeVI, one bioremediation approach would be to reduce the concentrations of SO4^2- (Lalvani, 2004; Yamani et al. 2014). A high concentration of SO4^2- is a common problem in mine effluents (Rodriguez et al. 2012) and therefore there are numerous methods for the reduction of SO4^2- (Kaksonen and Puhakka, 2007; Gadd, 2009; Rodriguez et al. 2012). One of the primary methods for reducing the concentration of SO4^2- is the biological reduction of SO4^2- using SO4^2- -reducing bacteria (SRB) in a passive anaerobic respiration process (Kaksonen and Puhakka, 2007). Other methods include passive reactive barriers and anaerobic ponds and the more effective, but costly, active treatment system of bioreactors (Kaksonen and Puhakka, 2007; Gadd, 2009; Rodriguez et al. 2012). Due to the similar chemical properties of SeVI and SO4^2-, Lalvani (2004) suggested a two-step immobilization approach for drain water to reduce both SO4^2- and SeVI, by removing SO4^2- with barium chloride (BaCl2) and using nanoparticles of NiFe to reduce the concentrations of SeVI. For industries with excess SeVI and high levels of SO4^2-, the primary action should be to reduce the levels of SO4^2- before attempting the biosorption of SeVI.

In contrast to SO4^2-, our data demonstrate that NO3 had no effect on the biosorption of SeVI by GMB despite concentrations of NO3 ranging between 0.02 and 434.03 mg L\(^{-1}\) and being 1500 times higher than the concentration of SeVI. The lack of competition between SeVI and NO3 for biosorption was not due to a lack of affinity between NO3 and the GMB. Indeed, GMB had a higher affinity for NO3 than SeVI and SO4^2-. Other studies have also found that NO3 has very little effect on the biosorption of SeVI (and other oxyanions such as As^V) from solution by iron-modified biosorbents (Lalvani, 2004; Zhang et al. 2005; Ansone et al. 2013). This lack of interference suggests that NO3 may adsorb to iron-modified biosorbents through different mechanisms to target oxyanions. Previous studies suggest that, unlike other dissolved oxyanions, ligand exchange is not an important mechanism for binding of NO3 to ferric oxides in aquatic systems (Yates and Healy, 1975). Interestingly, it has also been noted that concentrations of dissolved NO3 of 5 mg L\(^{-1}\) and above can inhibit the reduction of SeVI to Se0 in ground water (Bailey et al. 2012). Therefore, SeVI and NO3 may interact in the dissolved phase to alter the speciation and, therefore, availability of SeVI for biosorption. Regardless, our data support the view that not all oxyanions are problematic and that it will be necessary identify oxyanions which can interfere with biosorption of target element for each new water source. To this end, the performance of biosorbents must be evaluated in real-world effluents to truly assess their ability to treat target contaminants effectively.

5. Conclusion

GMB is an efficient biosorbent for SeVI in mock solutions and can successfully remove 98% of the SeVI present and achieve a maximum biosorption capacity (q\(_{\text{max}}\)) of 3.80 mg SeVI removed g\(^{-1}\) GMB. In contrast, the biosorption capacity of GMB to SeVI in a mine effluent is significantly reduced due to the presence of the oxyanion SO4^2-. The antagonistic relationship between SeVI and SO4^2- shows that any bioremediation of SeVI in an effluent with high levels of SO4^2- will be unsuccessful unless the levels of SO4^2- are reduced. Under the current mine conditions, with 108 µg L\(^{-1}\) SeVI and 640 mg L\(^{-1}\) SO4^2-, a reduction of 99% of the available SO4^2- by the GMB is needed to achieve a considerable reduction of SeVI. Conversely, high levels of the oxyanion NO3 do not impair the biosorption of SeVI by GMB despite the biosorption capacity of NO3 to GMB being higher than that of SeVI and SO4^2-. This study clearly demonstrates that, although valuable in understanding kinetics, results and conclusions drawn from a single-element mock experiment are of little use in predicting the performance of biosorbents in real-world effluents when competing compounds are present. Further research should focus on the performance of prospective biosorbents in real-world effluents so the interactions between target and non-target compounds can be better understood. Experiments should also consider how the production process of iron-modified biosorbents, such as the pyrolysis conditions employed, can be optimized to improve the affinity of these biosorbents for target oxyanions in waste water.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2014.11.031.

Author contributions statement

The paper was written by CLJ, DAR, NAP and R de Nys. CLJ and DAR wrote the main manuscript text and prepared figures. All authors reviewed the manuscript.

Additional information

The authors declare that no competing financial interests exist.

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