



Research article

Simultaneous biosorption of selenium, arsenic and molybdenum with modified algal-based biochars



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ABSTRACT

Ash disposal waters from coal-fired power stations present a challenging water treatment scenario as they contain high concentrations of the oxyanions Se, As and Mo which are difficult to remove through conventional techniques. In an innovative process, macroalgae can be treated with Fe and processed through slow pyrolysis into Fe-biochar which has a high affinity for oxyanions. However, the effect of production conditions on the efficacy of Fe-biochar is poorly understood. We produced Fe-biochar from two algal sources; “*Gracilaria* waste” (organic remnants after agar is extracted from cultivated *Gracilaria*) and the freshwater macroalgae *Oedogonium*. Pyrolysis experiments tested the effects of the concentration of Fe³⁺ in pre-treatment, and pyrolysis temperatures, on the efficacy of the Fe-biochar. The efficacy of Fe-biochar increased with increasing concentrations of Fe³⁺ in the pre-treatment solutions, and decreased with increasing pyrolysis temperatures. The optimized Fe-biochar for each biomass was produced by treatment with a 12.5% w/v Fe³⁺ solution, followed by slow pyrolysis at 300 °C. The Fe-biochar produced in this way had higher a biosorption capacity for As and Mo (62.5–80.7 and 67.4–78.5 mg g⁻¹ respectively) than Se (14.9–38.8 mg g⁻¹) in single-element mock effluents, and the Fe-biochar produced from *Oedogonium* had a higher capacity for all elements than the Fe-biochar produced from *Gracilaria* waste. Regardless, the optimal Fe-biochars from both biomass sources were able to effectively treat Se, As and Mo simultaneously in an ash disposal effluent from a power station. The production of Fe-biochar from macroalgae is a promising technique for treatment of complex effluents containing oxyanions.

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1. Introduction

Coal-fired power generation is a water-intensive industry that produces contaminated waste water. For example, the average 1000 MW coal-fired power station in Australia produces 0.5 billion L of “Ash Water” (AW) each year (Jankowski et al., 2006; Ruhl et al., 2009; Smart and Aspinall, 2009). While alternatives to water-based ash disposal, and recycled water, may be used at some power stations, it has nevertheless been shown that the use of water to dispose of coal ash can compete directly with the supply of water for basic human requirements (Smart and Aspinall, 2009; Faeth et al., 2014). Consequently, sustainable water treatment techniques are urgently required to reduce water pollution from energy production. However, the treatment of AW poses a particular

challenge as it is characterized by a very high concentration of metalloids that are encountered as oxyanions, all of which are difficult to treat through conventional processes (Kidgell et al., 2014a, 2014b; Roberts et al., 2015a). In particular, AW effluents have high concentrations of selenium (Se), arsenic (As) and molybdenum (Mo) in oxidized states (Jankowski et al., 2006; Roberts et al., 2015a).

Se is an essential element in trace amounts for all vertebrates; however, it can impair the function of enzymes in vertebrates at concentrations slightly in excess of essentiality (Hamilton, 2002). Se is typically present as the selenate oxyanion (SeO₄²⁻) in oxygenated waste water (Torres et al., 2011) and this form of Se has been implicated in cases of severe ecotoxicity to aquatic life in watersheds containing AW dams (Hamilton, 2004). In contrast, As has no biological function in vertebrates and is a known carcinogen and is highly toxic at low doses (Sharma and Sohn, 2009). Like Se, As is typically present as the arsenate oxyanion (AsO₄³⁻) in waste water (Sharma and Sohn, 2009). Mo is an essential trace element

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for most plants and animals as an enzymatic co-factor (Giussani, 2011). Mo is typically present as the oxyanion molybdate (MoO_4^{2-}) in AW at concentrations several orders of magnitude higher than other contaminants (Jankowski et al., 2006). While comparatively non-toxic to most vertebrates (relative to Se and As), high concentrations of Mo in drinking water and feed can have debilitating effects on ruminants leading to the fatal condition of molybdenosis (Giussani, 2011). For this reason AW cannot be re-used for irrigation until Mo is removed and Australian coal-fired power stations are often regulated against irrigation water quality standards for AW discharge.

High concentrations of Se, As, and Mo in effluents present significant problems to any remediation effort as conventional treatment technologies such as biosorption with Activated Carbon have no affinity for these elements in their oxidized forms (Mondal et al., 2004; Sappington, 2002). Similarly, while algal-based biosorbents are a proven technique for treatment of metals, they also have limited or no affinity for oxyanions unless they are specifically modified to enhance their ability to adsorb these contaminants (Kidgell et al., 2014a). One promising technique to enhance the biosorption of oxyanions is to treat biosorbents with iron (Fe) (Dobrowolski and Otto, 2013). Macroalgae are a particularly effective biomass for the production of Fe-based biosorbents. For example organic waste residues that remain after agar has been extracted from commercially cultivated seaweeds (*Gracilaria* spp.) (Roberts et al., 2015b), and green freshwater macroalgae cultivated in carbon capture ponds at coal-fired power stations (*Oedogonium* spp.) (Roberts et al., 2013; Ellison et al., 2014; Roberts et al., 2015a) have both proven to be effective biomass sources for Fe-based biosorbent production. Both of these biomass sources are particularly effective as they can be coated in a ferric chloride (FeCl_3) solution then converted into Fe-biochar through slow pyrolysis (Roberts et al., 2015b). Slow pyrolysis is the combustion of organic matter at high temperatures with oxygen limitation, which encourages the material to degrade into a recalcitrant charcoal (Lehmann and Joseph, 2009).

While algae are an effective feedstock for the production of Fe-biochar, the production process has not been explored in depth. Specifically, the effects of Fe-treatment in combination with pyrolysis conditions on the biosorbent capacity of Fe-biochar have not been tested in detail (Chen et al., 2011). Given the very different characteristics of waste residues from agar-extracted seaweeds (particularly the low C content of the seaweed wastes) and algal biomass it is likely that optimal production conditions vary for different source biomass. In addition, while it is known that pyrolysis conditions (particularly temperature) strongly affect the physical characteristics of un-modified biochar (without Fe) (Lehmann and Joseph, 2009), and consequently their affinity for dissolved metals when used as biosorbents (Wnetrzak et al., 2014), it is not known how these factors interact to affect oxyanion biosorption by Fe-biochar.

Therefore, in this study we use two sources of biomass to produce Fe-biochar for the optimized removal of dissolved oxyanions from a coal-fired power station AW effluent. The two biomass sources are “*Gracilaria* waste” (the residual biomass remaining after agar has been extracted from commercially cultivated *Gracilaria*, hereafter GW) and biomass of a green freshwater macroalga (genus *Oedogonium*). The primary aim of the study is to investigate the effects of production conditions on the capacity of Fe-biochar to remove the oxidized forms of Se, As, and Mo from waste water. First, we examine for each biomass how interactions between two factors; the concentration of Fe^{3+} in the pre-treatment solution, and the pyrolysis temperature at which the Fe-biochar is produced affect the capacity to adsorb Se. Second, using the Fe-biochar optimized for the adsorption of Se for each biomass, we quantify

its relative affinity for Se, As, and Mo which are all common constituents of AW effluents. Finally, we test the performance of the optimized Fe-biochar for each biomass in a real-world coal effluent from a coal-fired power station AW dam.

2. Methods

2.1. Biomass preparation

GW as de-alginate *Gracilaria* was obtained from AgarIndo Bogatama in Indonesia (Roberts et al., 2015b). AgarIndo Bogatama is an agar producing company that sources *Gracilaria* biomass from Indonesian open-ocean seaweed farms for the extraction and refinement of agar. AgarIndo Bogatama currently produces 90 tonnes of GW each month from this process. Agar is extracted from *Gracilaria* by first exposing the biomass to hot alkaline water (NaOH), then boiling the biomass and separating the agar from residual biomass with perlite-facilitated flotation. Samples of the GW (which accounts for approximately 60% of the original *Gracilaria* biomass weight) were sun-dried in Indonesia and sent to James Cook University, Townsville, Australia in July 2013.

The freshwater macroalgal biomass (genus *Oedogonium*) was initially collected from the AW dam at Tarong power station in Queensland, Australia (26°46'51" S, 151°54'45" E) in October, 2012. The biomass was cultured in outdoor facilities at the Centre for Macroalgal Resources and Biotechnology, James Cook University, Townsville, Australia (19°19'44" S, 146°45'40" E) in de-chlorinated water with the addition of Manutec water soluble f/2 algal growth media (Manutec MAF media) at 0.1 g L⁻¹. The cultures were harvested weekly and the biomass was sun-dried to a constant weight. Both biomass sources were rinsed with de-ionized water and dried in an oven at 60 °C for 24 h prior to use.

2.2. Production of Fe-biochar

Manipulative pyrolysis experiments were performed to investigate the effects of the concentration of Fe^{3+} and pyrolysis temperatures on the performance of Fe-biochar produced from GW and *Oedogonium*. GW and *Oedogonium* biomass were soaked in one of four FeCl_3 solutions equivalent to 1.5, 4, 8 and 12.5% Fe^{3+} w/v (equivalent to 1.5, 4, 8 and 12.5 g Fe^{3+} per 100 ml⁻¹, respectively) and these dilutions were obtained by diluting a 45% FeCl_3 solution (Sigma Aldrich) with deionized (DI) water. Each biomass was exposed to the Fe^{3+} solution for 24 h at 20 °C on a shaker plate (75 rpm) at a density of 25 g biomass L⁻¹ Fe^{3+} solution. The Fe-treated biomass was then separated from the FeCl_3 solutions by coarse filtration and rinsed with DI water until the rinsate ran clear. The rinsed Fe-treated biomass was then oven dried to a constant weight (24 h, 60 °C) and converted to Fe-biochar by slow pyrolysis as follows. Each Fe-treated biomass sample was weighed into mesh bags and placed in a stainless steel retort inside a muffle furnace. The muffle furnace was pre-heated to one of three target Highest Heating Temperatures (HHT; 300, 450 and 750 °C) and the retort was placed inside the furnace and purged with analytical grade N_2 gas at a flow rate of 4 L min⁻¹ for 60 min at the designated pyrolysis temperature. After 60 min the retort was removed from the muffle furnace and left to cool to room temperature under N_2 gas flow. The Fe-biochar was weighed to quantify yield as a percentage of the original Fe-treated biomass weight.

2.3. Effects of Fe-biochar production methods on biosorption capacity for Se

Each of the Fe-biochars produced as described above were tested for biosorption of Se in a 0.1 mg L⁻¹ and a 200 mg L⁻¹ Se

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