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Bioremediation for coal-fired power stations using macroalgae

David A. Roberts [a,*], Nicholas A. Paul [a], Michael I. Bird [b], Rocky de Nys [a]

[a] MACRO – the Centre for Macroalgal Resources and Biotechnology, College of Marine and Environmental Sciences, James Cook University, Townsville 4811, Australia

[b] Centre for Tropical Environmental and Sustainability Sciences, College of Science, Technology and Engineering, James Cook University, Cairns 4870, Australia

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ABSTRACT

Macroalgae are a productive resource that can be cultured in metal-contaminated waste water for bioremediation but there have been no demonstrations of this biotechnology integrated with industry. Coal-fired power production is a water-limited industry that requires novel approaches to waste water treatment and recycling. In this study, a freshwater macroalga (genus *Oedogonium*) was cultivated in contaminated ash water amended with flue gas (containing 20% CO_2) at an Australian coal-fired power station. The continuous process of macroalgal growth and intracellular metal sequestration reduced the concentrations of all metals in the treated ash water. Predictive modelling shows that the power station could feasibly achieve zero discharge of most regulated metals (Al, As, Cd, Cr, Cu, Ni, and Zn) in waste water by using the ash water dam for bioremediation with algal cultivation ponds rather than storage of ash water. Slow pyrolysis of the cultivated algae immobilised the accumulated metals in a recalcitrant C-rich biochar. While the algal biochar had higher total metal concentrations than the algae feedstock, the biochar had very low concentrations of leachable metals and therefore has potential for use as an ameliorant for low-fertility soils. This study demonstrates a bioremediation technology at a large scale for a water-limited industry that could be implemented at new or existing power stations, or during the decommissioning of older power stations.

1. Introduction

The majority of global energy is produced through the combustion of coal, and the growth of coal-fired power generation continues to outpace growth in power generation from all non-fossil fuel sources combined (IEA, 2013). In addition to being a source of carbon (C) emissions, coal-fired electricity production is a water-intensive industry that produces large quantities of waste water. A typical 1000 MW power station produces half a billion liters of metal-contaminated waste water each year (Smart and Aspinall, 2009). Increasing water scarcity threatens energy security and in some parts of the world (e.g. Australia, the United States, India and China) water supply for coal-fired power stations and for human consumption will be in direct competition within the next decade (Faeth and Sovacool, 2014; Faeth et al., 2014; Pan et al., 2012; Smart and Aspinall, 2009). Climate change due to C emissions is the most widely publicized environmental issue associated with coal-fired power generation. However, the direct conflict between water requirements for electricity generation and basic human needs is an under-appreciated societal and environmental issue that will play out in the near future.

One waste water stream produced at coal-fired power stations is "Ash Water" (AW) which is produced when water is used to dispose of residual ash left behind after the combustion of coal. A wide range of potentially toxic elements leach from ash into AW and this effluent contains high concentrations of many elements (e.g. Se, As, Al, and Cr) in excess of water quality criteria (Ellison et al., 2014; Roberts et al., 2013; Saunders et al., 2012). Consequently, AW is unable to be discharged and is typically stored in "Ash Dams" (AD) which poses a threat to watersheds and represents an inefficient use of scarce water resources in arid regions (Roberts et al., 2013). It is estimated that there are 1200 new coal-fired power stations under construction globally with a combined capacity of 1.5 million MW (Yang and Cui, 2012). These new power stations will produce up to 750 billion L of additional AW annually, effectively doubling the annual global production of AW in the next decade. Few

* Corresponding author.
E-mail address: david.roberts1@jcu.edu.au (D.A. Roberts).

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treatment options exist for AW and as such it is also a legacy contaminant that poses a persistent threat after power stations are decommissioned (Oman et al., 2002).

One approach to the bioremediation of AW is to use live macroalgae to sequester contaminants from the effluent (Roberts et al., 2013). Macroalgae – large, multicellular algae – can sequester dissolved metals through a two-phase process, with the metals first being passively bound to the cellular surface followed by active transport of metals across the cell membrane to be stored in intracellular storage vacuoles (Chojnacka, 2010). Once internalized, excess metals are sequestered by metal-binding pycho-chelatins that are produced by algal cells in response to high concentrations of metals (Pawlik-Skowrońska, 2001). These metal-protein complexes can then be stored in vacuoles to isolate metals from essential cellular processes and allow algae to store relatively high concentrations of some metals in an inert, detoxified form (Nishikawa et al., 2003; Volland et al., 2011). Furthermore, provisioning cultures with CO_2 from flue gas improves bioremediation through two concurrent processes. First, CO_2 supplementation in algal cultures circumvents C-limitation and therefore increases biomass productivity. Second, CO_2 supplementation alters the bioavailability of metals in AW by maintaining a lower pH of the water and, therefore, changing metal speciation (Roberts et al., 2013). While algal-based bioremediation has proven effective in the laboratory there is a view that it is unpredictable and too costly to apply at large scales. This is partly due to the fact that the complexities of culturing and harvesting microscopic microalgae have been under-appreciated (Pearman, 2013; Walker, 2009). In comparison, macroalgae are relatively easy to culture and harvest and this alternative feedstock for algal-based bioremediation must be demonstrated at scale to develop market acceptance.

Algal-based bioremediation could become more attractive if the biomass cultivated in bioremediation ponds could be used as a feedstock for the production of bioproducts (Shurin et al., 2013). The integrated cultivation of macroalgae with power stations overcomes constraints to the production of biomass by using non-arable land, non-potable water, and CO_2 emissions to support productivity (Fig. 1). The biomass could then be used in a diversity of end-uses, including as a feedstock for biochar production. Biochar is a carbon-rich charcoal produced through slow pyrolysis (the combustion of biomass under oxygen-limited conditions) (Lehmann and Joseph, 2009). Biochar contains recalcitrant C and an inorganic content capable of C sequestration and metal immobilisation (Lehmann and Joseph, 2009). Biochar is also used as a soil ameliorant to improve nutrient retention and to reduce emissions of greenhouse gases from soil (Cayuela et al., 2013). Slow pyrolysis also yields energy in the form of syngas as a by-product (Gaunt and Lehmann, 2008). Consequently, the intensive cultivation of macroalgae in conjunction with biochar production has the potential to deliver bioenergy with biological carbon capture and storage (Hughes et al., 2012). However, there is uncertainty regarding the suitability of biomass from bioremediation as a feedstock for production of biochar as pyrolysis has effects on the speciation and bioavailability of metals in biochar (Farrell et al., 2013).

In this study a world-first validation of large-scale macroalgal cultivation and bioremediation is conducted at an Australian coal-fired power station demonstrating a sustainable means of producing biomass for value-added applications. First, the productivity of biomass, the bioremediation of AW and biological C capture is quantified in ponds using a native species of freshwater macroalgae (genus *Oedogonium*). Second, biochar is produced from the biomass and its physico-chemical characteristics, suitability for soil amelioration, and ability to retain the metals accumulated by *Oedogonium* from the AW are assessed.

2. Materials and methods

This study was conducted at Tarong power station in Queensland, Australia (26°46′51″ S, 151°54′45″ E). Tarong has a current capacity of 700 MW, and a 46,000 ML (ML) AD containing AW contaminated with metals and metalloids during the disposal of ash. Tarong AW contains several elements that are in excess of the Australian and New Zealand Environment and Conservation Council (ANZECC) water quality guidelines, including Al, As, Cd, Cr, Cu, Ni, Se and Zn (Table S1).

2.1. The production of macroalgae

An endemic species of green freshwater macroalgae (genus *Oedogonium*, Genbank KF606974) (Lawton et al., 2014) was isolated from Tarong AD to inoculate cultures to evaluate bioremediation potential *in situ*. *Oedogonium* has a worldwide distribution and is a competitively dominant species that overgrows other algae under conditions of nutrient excess and has high productivity in monocultures (Lawton et al., 2014). *Oedogonium* is cultivated as a free-flowing suspended filament in large-scale cultivation (Cole et al., 2014). The Tarong *Oedogonium* isolate had individual filaments approximately 5 cm long and 200 μm in diameter. *Oedogonium* was isolated from the AD in October 2012 and then cultured to a large-scale (50 kg) in outdoor facilities at the Centre for Macroalgal Resources and Biotechnology, James Cook University, Townsville, Australia (19°19′44″ S, 146°45′40″ E). The biomass was transported to Tarong and cultured directly in AW which was pumped from the AD into a series of 15,000 L ponds with a longitudinal parabolic profile. The ponds had a maximum depth of 75 cm at the deepest point of the parabolic profile. The AW was passed through a 10 μm filtration unit to remove fine suspended ash from the waste water. Flue gas was piped from the power stations flue, into a desulfurization unit and then into the ponds. The flue gas supply was linked to a pH probe which was connected to a solenoid. When the pH probe detected that pH was above 8.6 in the ponds the solenoid activated the flow of flue gas until the pH decreased in the ponds to

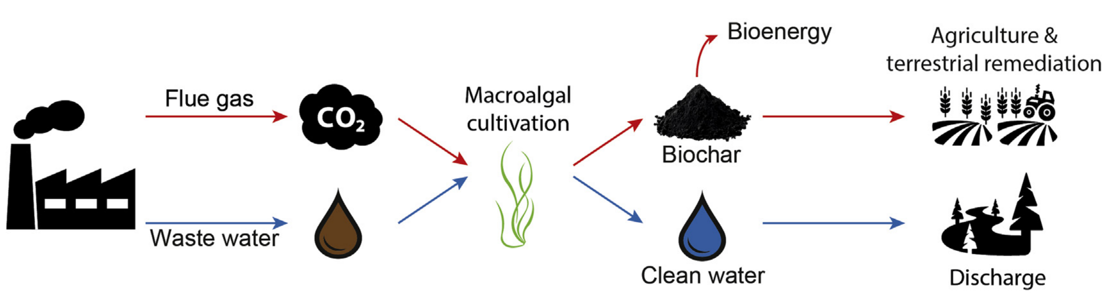

Fig. 1. Conceptual algal bioremediation model for coal-fired power stations.