Science of the Total Environment 442 (2013) 63–72

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Nutrient and dissolved organic carbon removal from natural waters using industrial by-products

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HIGHLIGHTS

► The CaO-based WTR effectively removed DOC and P in column trials and had a high P sorption capacity.
► Granular activated carbon attenuated organic contaminants but was unsuitable for P attenuation.
► Fly ash removed a suite of both inorganic and organic nutrients and DOC from water but released Se.
► By-products may mitigate eutrophication through targeted use in nutrient intervention schemes.

ARTICLE INFO

Article history:
Received 16 August 2012
Received in revised form 1 October 2012
Accepted 1 October 2012
Available online 21 November 2012

Keywords:
Water treatment residual
Eutrophication
Dissolved organic carbon
Water treatment

ABSTRACT

Attenuation of excess nutrients in wastewater and stormwater is required to safeguard aquatic ecosystems. The use of low-cost, mineral-based industrial by-products with high Ca, Mg, Fe or Al content as a solid phase in constructed wetlands potentially offers a cost-effective wastewater treatment option in areas without centralised water treatment facilities. Our objective was to investigate use of water treatment residuals (WTRs), coal fly ash (CFA), and granular activated carbon (GAC) from biomass combustion in *in-situ* water treatment schemes to manage dissolved organic carbon (DOC) and nutrients. Both CaO- and $CaCO_3$-based WTRs effectively attenuated inorganic N species but exhibited little capacity for organic N removal. The CaO-based WTR demonstrated effective attenuation of DOC and P in column trials, and a high capacity for P sorption in batch experiments. Granular activated carbon proved effective for DOC and dissolved organic nitrogen (DON) removal in column trials, but was ineffective for P attenuation. Only CFA demonstrated effective removal of a broad suite of inorganic and organic nutrients and DOC; however, Se concentrations in column effluents exceeded Australian and New Zealand water quality guideline values. Water treated by filtering through the CaO-based WTR exhibited nutrient ratios characteristic of potential P-limitation with no potential N- or Si-limitation respective to growth of aquatic biota, indicating that treatment of nutrient-rich water using the CaO-based WTR may result in conditions less favourable for cyanobacterial growth and more favourable for growth of diatoms. Results show that selected industrial by-products may mitigate eutrophication through targeted use in nutrient intervention schemes.

1. Introduction

Excess nutrient input to aquatic systems frequently results in eutrophication and ecosystem degradation. Attenuation of excess nutrients in industrial, urban, and agricultural wastewaters and stormwater is essential to safeguard aquatic ecosystems. Relatively low initial capital investment coupled with low ongoing operating and maintenance costs make constructed wetlands well-suited for wastewater treatment in developing countries, particularly in rural communities. Constructed wetlands for wastewater treatment generally demonstrate effective attenuation of N via denitrification, but are less efficient for P removal (Kivaisi, 2001). Whereas N removal is a microbially-mediated process, P removal is primarily due to sorption or precipitation reactions with solid media; thus, incorporation of materials with high P attenuation capacity into constructed treatment wetlands may substantially enhance P removal.

The chemical speciation of nutrients in wastewater may substantially influence the rate and mechanism of nutrient removal as well as their ultimate fate. Although inorganic N species may be expected to have a more immediate effect on phytoplankton growth, organic N can also impact aquatic productivity (Anderson et al., 2002; Seitzinger and Sanders, 1999; Seitzinger et al., 2002). Organic forms of nutrients may comprise a substantial proportion of the total nutrient load in some environments (Kroeger et al., 2006; Scott et al., 2007; Petrone et al., 2009), and often prove more recalcitrant in water treatment schemes (Abe et al., 2008; Sattayatewa et al., 2010; Werker et al., 2002). Dissolved organic N

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http://dx.doi.org/10.1016/j.scitotenv.2012.10.008

(DON) is frequently associated with dissolved organic carbon (DOC) transport and breakdown. The development of treatment systems with capacity for removal of both inorganic and organic forms of nutrients as well as DOC is required for treatment of wastewaters containing multiple chemical species of nutrients.

The ratio of nutrients within a water body is a significant factor in determining the potential for excessive algal growth. Excess P is often present in a water body during the process of eutrophication and N becomes the limiting nutrient. Many blue-green algae can fix atmospheric N, putting them at a competitive advantage when N is the growth limiting nutrient. The development of potentially toxic blooms of blue-green algae may be mitigated through substantial reduction in P input and shifting of the aquatic system toward P- rather than N-limitation, concomitant with a sufficient reduction in total nutrient concentrations.

In near-coastal environments, eutrophication may also be enhanced by Si deficiency through the growth inhibition of diatoms. Alterations to the proportions of Si, N and P which result in a Si:N ratio less than 1:1 may reduce diatom growth in favour of non-siliceous algae (Justić et al., 1995). Based on nutrient uptake kinetics, the following nutrient limitation criteria have been identified for diatom growth (Justić et al., 1995): potential N limitation where $N:P<10$ and $Si:N>1$; potential P limitation where $Si:P>22$ and $N:P>22$; and potential Si limitation where $Si:P<10$ and $Si:N<1$.

Constructed wetlands or similar structures which incorporate a reactive mineral phase for enhanced P, DOC and DON attenuation may be suitable for nutrient attenuation of wastewater in areas without access to centralised water treatment facilities. The use of low-cost, mineral-based industrial by-products with high Ca, Mg, Fe or Al content in constructed wetlands potentially offers a cost-effective wastewater treatment option. Industrial by-products have historically been viewed as unsuitable for use as environmental amendments due to the potential for contamination by hazardous constituents or to a lack of independent evidence indicating beneficial effect. Depending on their physico-chemical characteristics and nutrient sorption capacities some mineral-based industrial by-products may be suitable for the attenuation of nutrients in wastewater, thereby facilitating their productive use whilst reducing the environmental footprint of the associated industries. Drinking water treatment residuals (WTRs), coal fly ash (CFA) and granular activated carbon (GAC) produced from industrial or agricultural residues are low-cost, mineral-based by-products which may be suitable for use as sorptive media in constructed wetlands, drain liners, permeable reactive barriers or similar applications (e.g. Chen et al., 2007; Dias et al., 2007; Drizo et al., 1999; Gibbons et al., 2009; King et al., 2010; Oguz, 2005).

Worldwide, large quantities of WTRs are generated each year as a result of treatment processes to remove colour, turbidity and humic substances from drinking water. The coagulation agents used to treat water can include Fe and Al salts, organic polymers, CaO, $Ca(OH)_2$ and/or Mg-containing materials. Several factors have led to increased interest in re-use of WTRs including the implementation of increasingly restrictive environmental regulations for solid waste disposal, increased disposal costs and decreased landfill capacities.

Similarly, there is substantial interest in the beneficial re-use of CFA as a consequence of the enormous quantity of CFA generated annually and the associated disposal costs. Approximately 500 Mt of CFA, a fine-textured predominantly mineral residue, are generated each year as a residue from fossil fuel combustion in coal-fired power stations around the world (Ahmaruzzaman, 2010). On average, only about 16% of the CFA generated globally is utilised in a meaningful way (Ahmaruzzaman, 2010); thus, the majority of the CFA generated each year is disposed of in landfills, which has the potential to cause significant environmental degradation (e.g. Quispe et al., 2012; Silva et al., 2012a,b).

Activated carbon filters are widely used in water and wastewater treatment for the removal of synthetic organic chemicals and naturally-occurring organic chemicals. Activated carbon is generated when biomass is carbonized to charcoal and then activated with steam. Some industries generate activated carbon through integrated processes, and a number of agricultural and industrial by-products demonstrate potential as precursors for the manufacture of activated carbon products (Dias et al., 2007; Ioannidou and Zabaniotou, 2007).

The objective of this study was to investigate the use of selected low value, mineral-based industrial by-products in *in-situ* water treatment schemes to manage DOC and nutrients in contaminated waters. Mineral-based industrial by-products were investigated using a testing protocol which included physical, mineralogical, geochemical, and radiochemical characterisation. Nutrient and DOC attenuation by mineral-based industrial by-products was assessed in laboratory column trials and batch tests were used to quantify the P sorption capacity of each by-product. Low-cost materials incorporated into the testing program included: a CaO-based groundwater treatment residual; an iron-rich $CaCO_3$-based granular groundwater treatment residual; CFA from a coal-fired power station; and pre-commercial grade GAC resulting from wood combustion during electricity generation. Critical material performance indicators included nutrient and DOC uptake capacity, geochemical transformations and stabilisation.

2. Materials and methods

2.1. Column materials

Surface (0–15 cm) native Bassendean Sand for use in reference columns and as a nominally non-retentive phase in columns containing by-product mixtures was collected from the Swan Coastal Plain near Perth, Western Australia, and sieved to <2 mm to remove leaves and root fragments. The water treatment residuals used in these experiments were CaO- and $CaCO_3$-based materials used to remove colour and odour from groundwaters. Both the CaO-based WTR and the iron-rich, $CaCO_3$-based granular WTR were obtained from metropolitan groundwater treatment plants in Perth, Western Australia. Coal fly ash was sourced from a regional Western Australian coal-fired power station. Granular activated carbon from biomass combustion was obtained from an integrated eucalyptus tree processing plant in Western Australia. The CFA, and granular $CaCO_3$-based and CaO-based WTRs were oven dried to a constant mass at 105 °C, and the CaO-based WTR was ground to <63 μm particle diameter in a tungsten carbide ring mill prior to use in column experiments. The biomass-based GAC was used on an as-received basis.

2.2. Material characterisation

For each sample, the electrical conductivity (EC) was determined in a 1:5 solid to liquid (w/w) aqueous extract using deionised water, and by-product pH was determined in a 1:5 solid to liquid ratio (w/w) of 0.01 M $CaCl_2$ (Rayment and Higginson, 1992). Quantitative X-ray diffraction (XRD) analysis was used to characterise the mineralogical composition of by-products. The XRD patterns were recorded using Fe-filtered Co Kα radiation, a ¼° divergence slit, a ½° anti-scatter slit and a Si strip detector. Diffraction patterns were recorded in steps of $0.016°{\cdot}2\Theta$ with 0.4 s counting time per step. X-ray fluorescence analyses for major elements (as oxides) and trace elements were performed on fused glass disks and pressed powder pellets of each material, respectively, analysed on a wavelength dispersive XRF system.

2.3. Laboratory column experiments

Experimental materials were contained within stainless steel columns (1.0 m length with 2.2 cm internal diameter) with glass wool and a fine stainless steel mesh filter placed within fittings at each end of the columns to prevent blocking of column inlet or outlet.