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Removal of dissolved metals in wetland columns filled with shell grits and plant biomass

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ABSTRACT

Two lab-scale wetland systems were studied for the removal of dissolved Cu, Mn, Fe, Pb and Zn. Vegetated with *Typha domingensis*, each system consisted of two units, a vertical and a horizontal flow wetland column, which were filled with either crushed sea shell grits or composted green waste as main media. A synthetic acidic wastewater was prepared by dissolving H_2SO_4, $Pb(CH_3COO)_2$, $MnCl_2$, $FeSO_4$, $CuSO_4$ and $ZnSO_4$ in a distilled water. As it passed through each column, metal concentrations, pH and conductivity were monitored. The pH value of the wastewater increased in the shell grit columns, where dissolved metals were almost completely (> 99%) removed. In the wetland columns filled with the green waste, the average percentage removals were 90, 77, 27, 98 and 75% for Cu, Mn, Fe, Pb and Zn, respectively. Scanning electron microscopy and energy-dispersive spectroscopy (SEM-EDS) analysis showed that the surface characteristics of the shell grits remained largely unchanged before and after being used in the columns; but the mass compositions of carbon increased, whereas calcium and oxygen decreased. Infrared spectroscopy (IR) and X-ray diffraction (XRD) were used to further analyse the chemical compositions and functional groups of the surfaces of the shell grits.

1. Introduction

Mining and mineral processing activities often generate acidic wastewaters, such as drainage water from mine sites and seepage water from tailings and waste rock piles [1,2]. Metals in these acidic wastewaters tend to be in soluble forms, capable of penetrating to the groundwater or travelling long distances in surface waters [3]. These wastewaters are typically stored in open pits or dams for natural evaporation, a containment strategy that does not remove contaminants. Effective and cost efficient onsite treatment to remove the contaminants is a critical issue of water environment protection and risk mitigation.

Various active or passive technologies have been investigated for removing dissolved metals from polluted waters. Active treatment systems include sulfidogenic bioreactors [4], precipitation tanks [5], adsorption columns/beds [6], membrane filtration [7] and electrochemical systems [8]. Recent developments in nanotechnology [9] and biodegradable materials [10] have improved the competitiveness of some active systems, but they still have the disadvantages of relatively higher energy input and operating costs, and environmental incompatibility [11]. Passive technologies (such as constructed wetland, anoxic limestone drain, and permeable reactive barrier) are typically associated with lower operation and maintenance costs [12,13], which somewhat offset their disadvantage of large land requirement, in particular when the systems are in remote locations. Among the passive systems, constructed wetlands are known to be an effective ecological system.

Constructed wetlands have been studied for the removal of heavy metals from domestic wastewater [14,15], industrial effluents [16], leachate [17], storm runoff [18] and acid mine drainage (AMDs) [2]. In general, considerable percentage metal removals have been reported in the treatment of AMDs [19]. To date, most studies of acidic wastewater treatment using constructed wetlands have been conducted in the surface flow systems, sized largely based on hydraulic loading [20,21]. In subsurface flow systems, wastewaters filter through the packed media, instead of flowing over them. In theory, higher removal rates of dissolved metals (in mass removal per m^2 system surface) from the wastewaters are obtainable in the subsurface flow wetlands due to greater contact between the pollutants and wetland media, provided that adequate hydraulic conductivity is maintained [22,23].

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The predominant mechanisms of metal removal in the constructed wetlands are either biotic or abiotic, depending on system design and environmental condition. In a newly constructed subsurface flow wetland, the abiotic routes (e.g. sedimentation, flocculation, adsorption, ion exchange, precipitation and complexation) can remove the bulk of various pollutants within short retention time [14,24,25]. However, a wetland only has limited capacity to sustain the abiotic mechanisms; it may need extensive maintenance, or complete reconstruction, should its media become saturated with immobilised metals [26]. Biotic removal mechanisms (such as microbial transformations/immobilisation, plant uptake and harvesting) are sustainable routes of metal removal [4,27], provided that carbon, nutrients and suitable environmental conditions required by the microorganisms and plants are available [28].

The biotic and abiotic routes are both affected by the physio-chemical characteristics and quantity of wetland media [29]. The media supply the alkalinity and adsorption sites required for metal oxidation, precipitation and adsorption, and the surfaces and carbon sources for microorganisms (such as sulphur-reducing bacteria) to grow. The selection of wetland media is a critical factor that determines the effectiveness and life span [30] of a subsurface flow wetland when it is used to remove dissolved metals from wastewaters.

Gravel and sand are the traditional media employed in subsurface flow constructed wetlands [30,31]. However, these materials are unsuitable for removing dissolved metals, due to limited ability to increase alkalinity and facilitate precipitation. A variety of nonhazardous solid wastes have been studied in passive wastewater treatment systems; with mixed results reported in the literatures [32,33]. Examples of these solid wastes include alum sludge from drinking water treatment works [34], furnace steel slag [35], mining processing residue [34] construction waste [36], sugar cane bagasse [37], oyster-shell [21], coir husk chip [23], wood mulch [25,30], rice straw [38] and fragmented limestones [39]. Major advantages of using the nonhazardous wastes are two-folds: (a) enhanced pollutant removal efficiency due to suitable characteristics of selected materials, and (b) transformation of the solid wastes to resources. This study focused on the effectiveness of two nonhazardous solid wastes, crushed sea shells and composted urban green waste (primarily threaded woody plants), to remove dissolved metals.

2. Materials and methods

2.1. Synthetic wastewater

The chemical compositions of acidic wastewaters (such as mine drainage) vary significantly from site to site. In this study, a synthetic wastewater was prepared based on the characteristics of an effluent at a coal mining site [40], but with higher concentrations of copper and lead to allow the study of their removal. Measured amounts of $Pb(CH_3COO)_2$, $MnCl_2$, $FeSO_4$, $CuSO_4$ and $ZnSO_4$ powders, and H_2SO_4 solution was added in a distillate water, to produce a synthetic wastewater with target pollutant concentrations shown in Table 1. Under acidic condition, the metals were found to be primarily in dissolved forms.

Table 1
Chemical compositions and target metal concentrations in the synthetic wastewater.

	Theoretical concentration	Reagent used	Amount (g) per L water
Cu	4 mg/L	$CuSO_4(H_2O)_5$	0.01572
Fe	200 mg/L	$FeSO_4(H_2O)_4$	0.80287
Mn	18 mg/L	$MnCl_2(H_2O)_7$	0.08262
Pb	2 mg/L	$Pb(CH_3COO)_2$	0.00314
Zn	12 mg/L	$ZnSO_4(H_2O)_7$	0.05275
pH	2–3	H_2SO_4	

2.2. The lab-scale constructed wetlands

Two lab-scale wetland systems (operated in parallel) were installed outdoors (sheltered from rain). These two systems (namely, A and B) had identical configurations; each consisting of a cylindrical vertical flow column (A1 or B1) as the first treatment stage, followed by a rectangular horizontal flow column (A2 or B2) as the second stage, as shown in Fig. 1.

The bottom of each vertical flow column was filled with 15–30 mm round gravel to a depth of 10 cm, as a drainage layer. The same gravel was used in the water inlet and outlet sections (each being 50 mm long) of the horizontal flow columns to form inflow and outflow zones. The main spaces in the columns were filled with crushed sea shell grits (in system A) or composted urban green waste (in B). Some general characteristics of these media are described in Table 2.

Mature plants of *Typha domingensis* were collected from a creek on James Cook University's Townsville campus and re-planted in these columns. This species was selected due to its ability to tolerate low pH and adaptability to the local tropical climate. The plants were given two weeks to establish in the columns, prior to the commencement of experiments.

2.3. System operation, sampling and analysis

From a feed storage tank, two litres of the synthetic wastewater were collected and dosed manually to the top of the vertical flow column of each system; the effluent flowed by gravity towards the inlet zone of the horizontal flow column, before overflowing into an effluent collection tank. The manual dosing was done four days per week (Monday–Thursday). In total, eight litres of wastewater were dosed into each system per week; giving an average hydraulic loading rate of $0.252\ m^3/m^2\ d$ (m^2 represents surface area) on each vertical flow column, or $0.036\ m^3/m^2\ d$ on each horizontal flow column.

Water samples were collected on a weekly basis, every Thursday from the feed tank and outlets of the vertical flow columns, and every Friday from the effluent tanks. Immediately after collection, the samples were filtered through 0.45 μm syringe filters. The temperature, conductivity and pH values of the filtered samples were measured using a sensION MM374 measuring kit (Hach). The analyses of dissolved Cu, Fe, Mn, Pb, and Zn concentrations were carried out in the Advanced Analytical Centre at James Cook University using an inductively coupled plasma mass spectrometer (ICP-MS). Unused shell grits, together with used grits from the upper part of column A1, were sent to Edith Cowan University for SEM-EDS, XRD and IR analyses, using a scanning electron microscope (JCM-6000, JOEL), X-ray Powder Diffraction apparatus (PANAnalytical), and Spectrum Two IR Spectrometer (Perkin Elmer), respectively.

3. Results

3.1. Overall performance

A total of 40 water samples (including 8 influent samples from the feed tank, and 32 effluent samples from the first and second stages of the two systems) were collected and analysed. Table 3 presents the average data from each treatment stage, and overall removal percentages of dissolved metals. Higher dissolved pollutant removal percentages ($> 99\%$) were obtained in system A than in system B, primarily due to the high removal efficiency obtained in the first stage VF column (A1).

Temperature, pH and conductivity all three parameters of the synthetic wastewater were stable in the sample collection period, as indicated by their low standard deviation values in. However, as the synthetic wastewater passed through the systems, the change of pH values were significantly different in systems A and B; this being the primary factor for the discrepancies in metal removal efficiencies in the two systems.