Use of marine and engineered materials for the removal of phosphorus from secondary effluent

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A B S T R A C T

Constructed wetlands (CWs) require large area per population equivalent for the treatment of domestic wastewater. Hence, more compact CWs with equivalent or higher treatment efficiency per m^2 than conventional CWs need to be developed. The aim of this study was to reduce the required area by enhancing the phosphorus removal through the use of marine (i.e., crushed coral, oyster-shells and mussel-shells (raw and pyrolyzed)) and engineered (i.e., nanoparticle–beads) materials. This was done in batch and column experiments.

The pyrolyzed materials and the nanoparticle–beads showed a phosphorus removal capacity exceeding 99%, respectively through precipitation and adsorption. The conditions each material needed for the removal were different (e.g., contact times and material-to-solution ratios). Conversely, the raw marine materials did not achieve high removal efficiencies (12–59% after 7 days), unless the pH was increased to approximately 12. In general, all materials achieved phosphorus-removal levels beyond typical CW, the pyrolyzed materials and nanoparticle–beads being the most effective of the materials investigated. However, the high pH ($\sim$12) of the effluent after the treatment with pyrolyzed material can be a limitation of its application. A (separate) post-CW filter, packed with either pyrolyzed materials or nanoparticle–beads is proposed to increase the phosphorus removal efficiency thereby reducing the total space requirement of a CW. Recommendations for practical use are also included in this study.

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1. Introduction

Phosphorus, mainly from untreated wastewater, has been identified as the main contaminant causing algal blooms and subsequent eutrophication in water bodies (Rittmann et al., 2011; Metcalf and Eddy, 2003). Concentrations as low as $100\,\mu g\,L^{-1}$ still provide sufficient nutrients to cause eutrophication (Bitton et al., 1974). At the same time, phosphorus is a non renewable resource, well used in industry and agriculture, predicted to dwindle in the next fifty years (Sengupta and Pandit, 2011). Hence, phosphorus present in wastewater should be recovered and reused.

Constructed wetlands (CWs) are not usually effective in removing phosphorus (Prochaska et al., 2007; Arias and Brix, 2005; Lüderitz and Gerlach, 2002), seldom achieving residual phosphorus concentrations below the limits that can avoid eutrophication. Although CWs are recognized as an efficient natural wastewater treatment system, their poor phosphorus removal efficiency is still a hurdle for wider application.

The main removal mechanisms of phosphorus in CWs are plant uptake, precipitation and adsorption. The amount of phosphorus removed when harvesting the plants is small ($2–4.9\,g\,P\,m^{-2}\,year^{-1}$) as compared to the amount of phosphorus entering wetlands via wastewater (typically $150–300\,g\,P\,m^{-2}\,year^{-1}$) (Kadlec and Wallace, 2009; Arias et al., 2001). Phosphorus can be precipitated by Mg^{2+}, Fe^{3+}, Fe^{2+}, Al^{3+} and Ca^{2+} cations to form insoluble compounds (Rittmann et al., 2011). In CWs, a filter medium with a high content of these cations can thus be used to enhance precipitation and to increase adsorption sites. However, results are not yet satisfactory: phosphorus is not removed sufficiently to avoid eutrophication; phosphorus recovery is rather difficult; and eventually media saturation will occur. To increase the CW efficiency aiming for phosphorus removal, commonly a larger system is used (more media and therefore, more adsorption sites). This may temporarily enlarge the system's life span but will introduce the disadvantage of a larger footprint. For these reasons, it is recommended to have a compact and external phosphorus post-treatment step that serves as a polishing function for a CW and also provides the opportunity to recover phosphorus without expanding the system size.

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This study tests the suitability of marine and engineered materials for the post-treatment of phosphorus from secondary effluent (e.g., from CWs). The marine materials (e.g., oyster- and mussel-shells) are a renewable source of $CaCO_3$ and some are available on the seashore or as a waste product of shellfish farms (Abeynaike et al., 2011). The engineered material is a phosphate selective resin dispersed with iron oxide nanoparticles (iron content of 75–90 mg Fe g^{-1} resin), providing active adsorption sites for the removal of phosphates (Sengupta and Pandit, 2011).

Several tests were performed to understand the phosphorus removal mechanism of the materials investigated and to determine their capacity, mode of use and application in CWs. This study specifically aimed to: (i) assess the phosphorus removal efficiency of the selected materials, (ii) ascertain the phosphorus removal mechanism of the marine material (after pyrolysis) and (iii) propose an efficient phosphorus removal material (with some practical recommendations) that can improve the phosphorus treatment provided by CWs, thereby avoiding the costly need to oversize for sufficient phosphorus removal.

2. Materials and methods

2.1. Tested material and phosphorus source

The tested phosphorus-sorbing materials were oyster-shells (OS), mussel-shells (MS), crushed coral (CC) and nanoparticle–beads (NB). To the authors' knowledge, this is the first study using NBs as a potential phosphorus polishing material for CWs. All materials, except for the NB, were used in two forms: natural (called "raw") and pyrolyzed under nitrogen gas at 750 °C for 1–2 h (called "pyrolyzed") according to Kwon et al. (2004). The source of phosphorus used in the study was a mono-phosphate solution ($\sim$30 mg P L^{-1}, pH$\sim$5, demineralized water spiked with KH_2PO_4) and domestic wastewater (DWW) ($\sim$10 mg P L^{-1}, pH$\sim$7, primary settled effluent from Harnaschpolder wastewater treatment plant, Delft, The Netherlands) (Table 1). It should be noted that the concentration used in the phosphate solution is above of what it is reported as high strength DWW in the literature (12 mg L^{-1} of total P, Metcalf and Eddy, 2003), but the intention was to assess the removal limits of the materials investigated.

2.2. Batch experiments

Batch experiments were conducted in duplicate using 500 mL plastic bottles containing a phosphorus source and 10 g of material. The bottles were capped and placed immediately in a shaker at 100 rpm for 7 days. For comparison reasons all the materials, except for the NB, were crushed to the same size (<0.3 mm). In

Table 1
Physico-chemical composition of the raw domestic wastewater used in this study.

Parameter	Unit	Value
pH	–	7.3 ± 0.3
Temperature	°C	14.3 ± 2.2
DO	mg L^{-1}	2.9 ± 1.8
EC	μs cm^{-1}	1273 ± 411.8
BOD_5	mg L^{-1}	134.5 ± 69.9
COD	mg L^{-1}	435 ± 12.3
DOC	mg L^{-1}	74.7 ± 31.7
TSS	mg L^{-1}	135.4 ± 69.1
NO_3^-–N	mg L^{-1}	0.3 ± 0.4
NH_4^+–N	mg L^{-1}	43.2 ± 17.5
PO_4^{3-}–P	mg L^{-1}	7.8 ± 2.8
E. coli	CFU 100 mL^{-1}	$6.2 \times 10^6 \pm 2.2 \times 10^6$
Total coliform	CFU 100 mL^{-1}	$22 \times 10^6 \pm 8.4 \times 10^6$
Alkalinity	mg L^{-1} as HCO_3^-	428.2 ± 13.8
Ca^{2+}	mg L^{-1}	65

some batch tests, silica sand (1–1.6 mm) was added to simulate a mixture with the CW matrix since sand is a substrate widely used in CWs. Depending on the batch test (with or without sand), one or two control bottles were included: (i) control, 500 mL of phosphorus source and (ii) control-sand, 450 mL of phosphorus source plus 150 g of sand. Each experiment consisted of the following sequential steps: filling the 500 mL plastic bottle with the phosphorus source, addition of sand (when required by the experiment), addition of the tested material, placement in the shaker and reaction period. The phosphate concentration and pH were measured and sampling was conducted at: T_0 (time zero, solution/wastewater alone), T_S (time zero–sand, immediately after the sand was added, if added), T_M (time zero–material, immediately after the material was added) and after 1 h, 1 day and 7 days.

The influence of the high pH on the raw marine material was tested. For that, a similar duplicate batch experiment was conducted using the phosphate solution mixed either with pyrolyzed or high-pH ($\sim$ 12, adding 10 M NaOH) raw marine material. Two control bottles were used: (i) control (phosphorus source only) and (ii) control-pH (phosphorus source with high pH). The sampling regime was conducted at $T_0, T_{M\&adjustedpH}$ (time zero–material immediately after the pH modification) and after 1 h, 1 day and 15 days.

2.3. Column experiments

Sand, NB and OSs (pyrolyzed and raw) were selected to build nine columns of 2.5 cm internal diameter and 15–30 cm depth according to Table 2. To avoid cementation in the OS columns, the packing material consisted of 3–5 mm beads and was manually prepared (Supplementary data S1). The columns were saturated with DWW in a down flow mode and the outlets were adjusted to a flow rate of 0.5 mL min^{-1}. Between the material and the outlet pipe, a piece of glass wool was used to avoid loss of the material. Influent and effluent water samples were analyzed for pH and PO_4^{3-}–P during 2 months (daily and weekly during the first and second month, respectively): 7 days of startup period where diluted (5:1) DWW was applied and 54 days of experimentation period where raw DWW was used. Ca^{2+} ions were measured randomly in the raw ($n = 4$) and pyrolyzed ($n = 8$) material effluent.

2.4. Tests for pyrolyzed material phosphorus removal mechanism

The phosphorus removal mechanism of OS was tested by the Imhoff cone test (APHA, 2005) and the leaching test (norm 12457-2 from UNI EN, 2004). Two other tests were performed to further study the phosphorus removal mechanism. The first, the "solids/colloids experiment", consisted of adding 16.7 g of pyrolyzed OS (<0.3 mm) to two beakers containing 500 mL of demineralised water (material-to-solution ratio of 1:30), which were stirred for 1 h. One mixture was filtered (0.2 μm), the solids discarded and the liquid phase was kept. To both beakers, 1 L of phosphate solution was added and stirred for 1 h. Sampling was conducted after filtration, immediately, 30 min and 1 h after the addition of the phosphate solution. This experiment was done to evaluate whether the presence (or not) of solids and colloids (pyrolyzed OS) contributed to the removal of phosphorus.

To test if the phosphorus removal efficiency is linked to a high pH (needed for precipitation), a second test, the "titration experiment", was performed. For this experiment, the pyrolyzed OS was mixed with water to form a water-OS solution (0.25 g OS: 1 mL water). Sequential additions of 1 mL water-OS solution and drops of 0.5 M H_2SO_4 (to maintain the pH below 8, to avoid precipitation) were added to a beaker containing 1 L of phosphate solution. The water-OS solution was used to provide an instant