POTENTIAL FILTER MEDIA FOR NUTRIENT REMOVAL IN VERTICAL SUBSURFACE FLOW CONSTRUCTED WETLANDS

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ABSTRACT –**Potential filter media for nutrient removal in vertical subsurface flow constructed wetlands** Peat, coco products, light-weight expanded clay and lava rock are used as alternate filter media to treat domestic wastewater in on-site constructed wetlands. The aim of this study is to examine the nutrient removal by these media. Column studies and adsorption tests were used to establish the possible nitrogen and phosphorus removal caused by these filter media. None of the tested lignocellulosic filter media showed an efficient phosphorus removal in these experiments. Removal of total nitrogen was very limited for both peat and coco products. A good nitrification was evident in all the filter media. In non-buffered coco peat a small quantity of nitrate was adsorbed. Because calcium nitrate is used for buffering of coco products, this adsorption will only be present in non-buffered coco products. Of course the overall nitrate removal is negligible. The main mechanism for ammonium removal is nitrification. From a certain point nitrification slows down and consequently ammonium-N removal reduces proportionally. The light-weight expanded clay produced in Flanders (Argex), shows a good capacity for phosphorus sorption. Taking into account the typical dimensions and characteristics of a vertical subsurface flow constructed wetland ($3m^2/P.E.$; infiltration column 80cm) and the density of Argex, this means the constructed wetland will be saturated after approximately 20 months, assuming 1 P.E. stands for 2 mgP/d. Lava rock seems to be a very good substrate for nitrification. Phosphorus removal is limited but better than the filter media generally used in constructed wetlands.

Keywords Constructed wetlands; nutrients; peat; coco peat; coir pith , light-weight expanded clay, lava

INTRODUCTION

Discharge of wastewater is one of the major sources of nitrogen and phosphorus entering water bodies, causing undesired environmental problems such as eutrophication and algae bloom. Important sources of nutrient-pollution in Belgium and in other European countries are single households in rural areas discharging inadequately treated wastewater. These households have to rely upon on-site, low-cost small-scale wastewater treatment systems, for instance constructed wetlands (VYMAZAL J. ET AL. 1998). Constructed wetlands have proved to remove nutrients and different removal mechanisms taking place have been identified (KADLEC R. ET AL. 1996). In order to achieve efficient cost effective treatment systems, natural materials, e.g. sands, gravel, light-weight expanded clay, lava rocks, peat, coco products etc., are generally been applied as filter substrates in constructed wetlands.

In a vertical subsurface flow constructed wetland, a liquid phase and air are passed through the filter media, invoking the processes of adsorption and aerobic biological degradation of the nutrients in the liquid. The relative extent to which adsorption or biological degradation dominates in nutrient removal may vary with the filter substratum used, as well as with local conditions like pH and temperature. The interdependence of these processes is still unclear. Adsorption of solutes onto the surface of organic media may benefit or hinder their subsequent degradation by micro-organisms (MCNEVIN D. ET AL, 1998).

As a low cost, particulate medium, peat is an attractive and inexpensive option for the removal of colloidal and dissolved pollutants, although such advantages must be balanced against the importance of peatland conservation and the maintenance of habitat diversity. Peat can be described as partially fossilised plant matter which accumulates in wet areas where there is a lack of oxygen and the accumulation of the plant material is more rapid than its decomposition (COUILLARD D., 1994). Peat is a porous, complex material containing lignin, cellulose and humic acids as major constituents. These constituents contain polar functional groups, such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxyls, phenolic acids and ethers that can be involved in chemical bonding. Because of the polar character of peat, the specific adsorption potential for dissolved solids is quite high. Several studies have established the potential of peat to capture organic matter, nutrients, suspended solids, dissolved metals, oils and odors from domestic and industrial wastewater (BROWN P.A. ET AL., 2000). The particulate and highly porous nature of peat also makes it an effective physical filter. Studies have shown that partially decomposed peat has a relatively high porosity of approximately 95% and a specific surface area of 200 m^2 per g (HEADLEY T., 2006).

Coir is the name given to the fibre that constitutes the thick mesocarp or husk of the coconut (*Cocos nucifera*) fruit. This fibre is used for manufacturing ropes, matting and many other products. When the husk is processed, industrially valuable long fibres are removed leaving a considerable amount of both pith tissue and short- to medium-length fibres. These materials remain available as a waste product. Coir waste may be screened to remove part or most of the fibre. The light fluffy material, which is generated in this separation process is called coir pith or coco peat. This raw coir pith consists of 35% cellulose, 25.2 % lignin, 7.5% pentosans, 1.8% fat and resins, 8.7% ash content, 11.9% moisture content and 10.1% other substances. Coir pith was tested for the removal of many different contaminants: organic matter, nutrients, metals, dyes (NAMASIVAYAM C. ET AL., 2008).

Constructed wetlands that use lava rocks as filter material are widely used in Belgium for the treatment of water from swimming ponds and fish ponds. Lava biofilters are also used as a first stage in a multistage constructed wetland treating agricultural wastewater. In most cases the system works as a saturated filter reactor. These constructed wetlands are typically planted with *Iris pseudacorus*. They were never subject of accurate scientific research. Lava rocks are also an important filter material in trickling filters treating contaminated air.

Light-weight expanded clay aggregates (LWA) are presented by many authors as a possible medium for phosphorus (P) removal in constructed wetlands (DRIZO A. ET AL., 1999, BRIX H. ET AL, 2001, JOHANSSON L., 1998). Light-weight expanded clay aggregates are produced by the high temperature (up to ca. 1200°C) calcination of clay minerals. During the calcination in rotary kilns the organic matter in the clay expands, resulting in a high porosity mineral of low bulk density with higher hydraulic conductivities than similar sized sands and gravels. The results presented by the different authors suggest that the phosphate uptake capacity may vary over two orders of magnitude up to ca. 3.5 mg/g. The primary determinant of phosphate uptake is the total metal, and in particular Ca concentration (ZHU T. ET AL., 1997). Field evaluation demonstrated an efficient nitrification via adsorbed microbial biomass (HEISTAD A. ET AL., 2006).

The objective of this paper is to evaluate nutrient removal treating N- and P-solutions by percolation over different types of substrates. The filter media tested are all readily available in Flanders.

MATERIALS AND METHODS

Materials

Peat. The peat used was a mixture of 50% Irish peat and 50% Baltic peat. Irish peat is a more stable product, Von Post scale H3-H5. Baltic peat contains more fibres and is less decomposed, Von Post scale H1-H3. Two types were tested: an untreated mixture and a mixture treated with lime. Peat-based substrates are treated with lime to neutralize substrate acidity, increase pH buffering capacity, and provide calcium and magnesium.

Coco products. Three types of coco products were tested: coco chips, non-buffered coco peat, and buffered coco peat. Coco chips are produced by cutting the husk of the coconut into pieces. This results in a fibrous material with fibre sizes between 5 and 11 mm. The fibres are not washed. This product is used as a filter substrate in small on-site wastewater treatment systems in Belgium. Coco peat (or coir pith) is used as a growing medium for container-grown ornamental plants. Coco peat is always washed with water. 90% of the particles have a size smaller than 3 mm. Because coco peat has a negatively charged complex it is surrounded by positively charged ions primarily consisting of sodium and potassium. A buffering process can be applied to exchange sodium and potassium with calcium. During this process coco peat is treated with a solution of $Ca(NO_3)_2$.

Argex is a light-weight expanded clay aggregate produced in Flanders. The raw material used for this type of LWA is the Rupelian Boom clay. This type of clay has very distinct qualities (DECLEER J. ET AL., 1993). It is a suitable raw material since it contains components which liberate gases at a specific temperature and it has a chemical composition which produces a high temperature melt with a viscosity high enough to trap these gases. Although the composition of Rupelian Boom clay is far from ideal. Some parts of the clay deposit contain more organic matter than others. The presence of more than 3% organic matter has a negative influence on the expansion. In addition it is not clear why more iron has to be added to the Rupelian Boom clay in comparison with other European clays with a similar chemical composition. Industrial experience has shown that the addition of iron compounds facilitates the expansion process. During production a metallurgical waste product, containing ferric oxides is added. Ferric oxides are known to be capable of binding phosphorus strongly. However, since carbon is present in the raw material as organic matter, it is able to reduce the iron oxides. The expanded clay tested was the Flemish Argex 0-4. Grains of Argex are rough in appearance and rounded in shape. The surface of the grains is made up of a brown microporous crust. The interior of the grains has a black cellular texture. The grains were sized between 0 and 4 mm. The substrate contains 90 mg/g Al, 100 mg/g Fe, 14 mg/g Ca, 9 mg/g Mg.

The *lava stones* used in the test, originate from the volcanic Eifel region in Germany. It is a commercial product used as a filter material in pond filters and in drain layers on green roofs (Lavadrän 2/12 and 8/16, Vulkatec). This porous volcanic rock consists mainly of augite, olivine, limonite and biotite. Two different granulometries were tested, between 2 and 12 mm, between 8 and 16 mm. The substrate contains 53 mg/g Al, 84 mg/g Fe, 93 mg/g Ca, 84 mg/g Mg.

Batch studies

The maximum phosphate adsorption capacity was determined using a batch equilibrium technique as described by Seo (SEO ET AL. 2005).

Column studies

A pilot plant with infiltration columns was constructed. These columns were set up and operated as a vertical subsurface flow wetland (without macrophytes). The columns were applied with a solution containing NH_4NO_3 (45ppm N) and KH_2PO_4 (15 ppm P). The hydraulic loading was 50 $l/m^2.d$, the water was applied once a day. A daily sample was taken from the effluent of the columns, proportional to the quantity. These samples were tested for NH_4^+-N, NO_3^--N, total P, pH and conductivity.

Another pilot plant was built to determine the maximum adsorptive capacity of certain filter substrates for N or P. This pilot plant operates in exactly the same way, but other salt solutions were used (75 mgP/l, 150 mgP/l, 225 mgN/l, 450 mgN/l). In an identical set-up, the nitrification in lava stone was examined. Three columns were prepared. One column was filled with untreated lava 2/12. In another column lava 2/12 was used, cooked in water during 15 minutes prior to the test. Both columns were applied with a solution containing 22.5 mg NH_4^+-N/l and 22.5 mg NO_3^--N/l. To the influent of a third column packed with lava 2/12, a nitrification inhibitor was added, 15 mg/l allylthiourea.

Analytical methods

Total phosphorus was determined photometrically according to the phosphormolybdenum blue method (Spectroquant Phosphate Cell Test 14729). NH_4^+-N and NO_3^--N were analysed with ion specific electrodes (Symphony Electrodes). A calibration of the ion specific electrodes was performed before and after the analysis of the samples. pH was measured with a Symphony pH electrode, epoxy, gel, 3 in 1. Electrical conductivity was determined with a Hanna Instruments conductivity meter HI99300.

RESULTS AND DISCUSSION

Phosphorus

On average the removal percentages for total phosphorus were 5.6 % for coco chips, 12.0 % for buffered coco peat, 8.8 % for coco peat, 15.7 % for limed peat and 8.6 % for peat. From these results can be concluded that the adsorptive capacity for phosphorus of these lignocellulosic products is very low. There was no significant difference between the filter media ($\alpha = 0.05$). The higher calcium content of limed peat and buffered coco peat only results in a small increase of the adsorptive capacity. In the beginning of the column test with coco chips an important release of phosphorus was observed, which decreased during the first 3 weeks. This coincided with a decrease of the electrical conductivity and an increase of pH. The electrical conductivity changed from 3.66 mS/cm to 0.36 mS/cm, the pH from 6.59 to 7.58. Since this type of coco chips is not washed before use, solutes are washed out in the beginning of the treatment process.

After a test period of 20 weeks, the expanded clay showed an average reduction percentage of 76,2%, calculated from the mass balance. Two types of lava rock with different size distribution were tested, i.e. 2-12mm and 8-16mm. The first removed 48,3%, the latter 41,6%.

The adsorption experiments showed that P-adsorption in LWA followed the Langmuir isotherm. Using the Langmuir equation, the theoretical P adsorption capacity was calculated for two products: round Argex AR0/4 0.81 mgP/g and crushed Argex AG0/4 1.33 mgP/g. The crushed LWA showed a higher adsorption capacity since this product has a greater surface area. D10 of the crushed product is 0.063 mm, D60 1.00 mm, for the round LWA these values are 0.125 and 2.00 respectively. Because of the specific characteristics of Rupelian Boom clay, more iron has to be added to the clay to enhance the expansion process. This added Fe_2O_3 is an important factor in the P-sorption by Argex. Adsorption tests were performed on a product produced in a laboratory pilot plant under the same processing conditions but without adding Fe_2O_3. The LWA without addition of Fe_2O_3 could adsorb only 0,43 mgP/g. If the granules were glowed at 900°C, the maximum adsorption decreases to 0.20 mgP/g. This glowing process causes the formation of a rim of crystalline hematite surrounding the granule, hindering the adsorption of P inside the granule. Because the conditions during an adsorption test differ clearly from the conditions during an infiltration study, the maximum P adsorption was also determined using the infiltration columns. Calculated from these results, the maximum P-adsorption was found to be 0,650 mgP/g for Argex AR 0/4.

Nitrogen

With the exception of untreated peat, all the lignocellulosic filter media demonstrated a good removal of ammonium nitrogen (Table 1). There was no significant difference between the buffered and the non-buffered coco peat ($\alpha = 0.05$).

Table 1. Mean removal percentages.

	coco chips	coco peat buffered	coco peat	limed peat	peat	
Total Phosphorus	5,6	12	8,8	15,7	8,6	%
Total Nitrogen	6,5	10,2	23,9	0	0	%
Ammonium N	63,5	83,4	86	75,1	26,4	%

From the cumulated mass balances can be concluded that the removal of ammonium nitrogen was stable during the 30 weeks test period, except for coco chips (Figure 1).

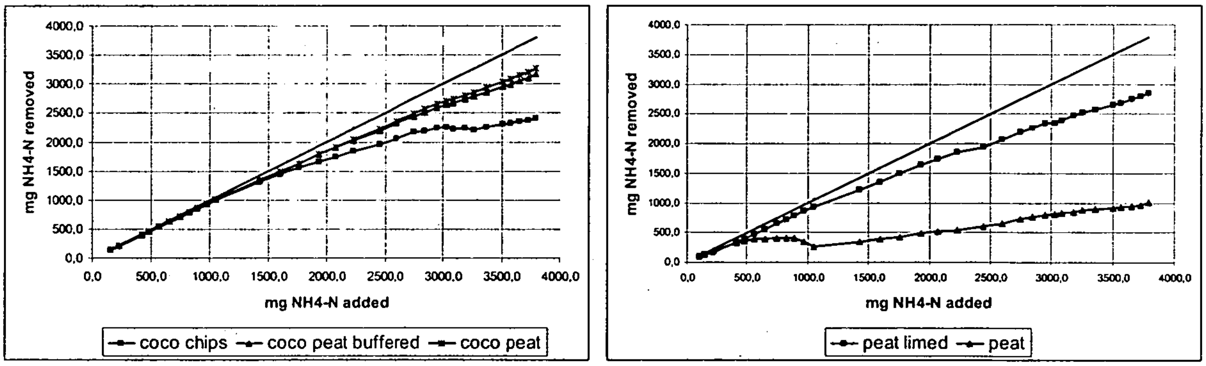

Figure 1. Cumulated mass balance for ammonium nitrogen, mg NH_4^+-N removed against mg NH_4^+-N added per column.

From the results of the nitrate analyses it was obvious that nitrification occurred in all the filter media, although the nitrification rate differed for the tested media. In the limed peat nitrification started after approximately one month. The untreated peat showed very slow nitrification due to the low pH of the medium (limed peat pH = 6.95, peat pH = 3.75). In the coco products nitrification started later compared to the peat products, after approximately 45 days. During this initial period the non-buffered coco peat was even able to adsorb nitrate (Figure 2).

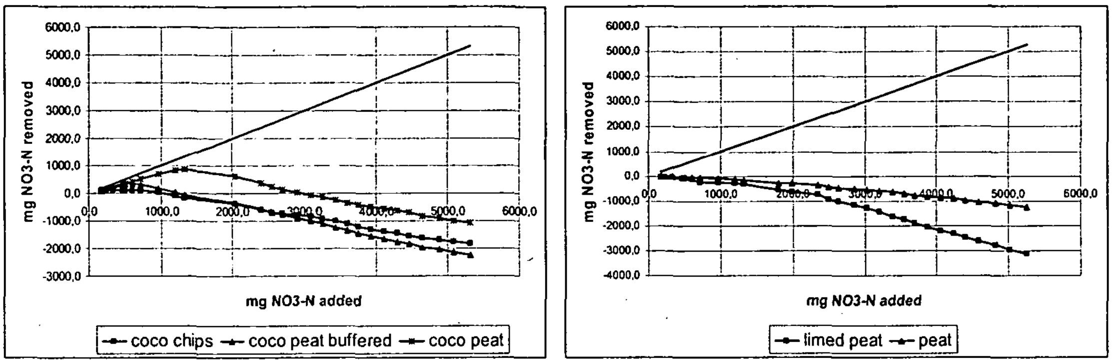

Figure 2. Cumulated mass balance for nitrate nitrogen, mg NO_3^--N removed against mg NO_3^--N added per column.

On average the removal percentages for total nitrogen were 6.5 % for coco chips, 10.2 % for buffered coco peat, 23.9 % for coco peat, 0.0 % for limed peat and 0.0 % for peat, as can be concluded from figure 3.

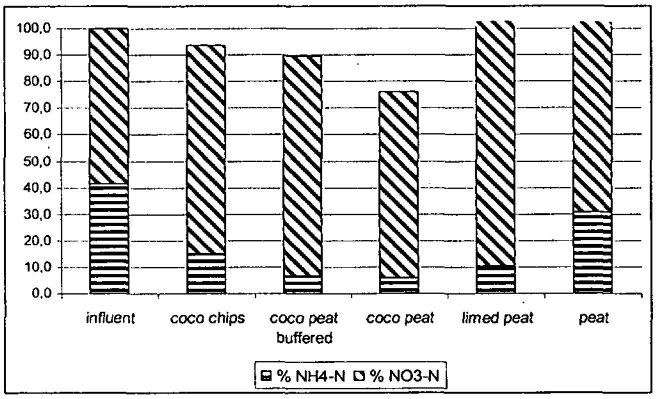

Figure 3. Ratio between ammonium-N and nitrate-N in terms of percentages.

Since both peat and coco products can be considered as negative complexes, positive ammonium ions can be adsorbed. Because non-buffered coco peat demonstrated the best ammonium removal, the nitrification and adsorptive capacity for ammonium was tested with NH_4NO_3-solutions of higher concentrations (TN: 225 mg N/l and 450 mg N/l). The results showed three different phases during nitrogen removal with non-buffered coco peat. In the first month nitrate-N is adsorbed (Figure 2) and ammonium-N was removed (> 96%). From the other results can be concluded that the nitrification process only starts after 30 to 45 days. This means the ammonium-N removal in this first phase can be attributed to adsorption. In a longer second phase ammonium-N was converted to nitrate-N, (ammonium removal = 50%). The third phase starts when approximately 2000 mg NH_4^+-N/kg substrate was removed. Both ammonium-N removal and nitrification approached almost zero (Figure 4). An important change in pH causes these phenomena. The pH decreases from 6.5 to 4.7. The low pH-conditions inhibit the growth of nitrifiers.

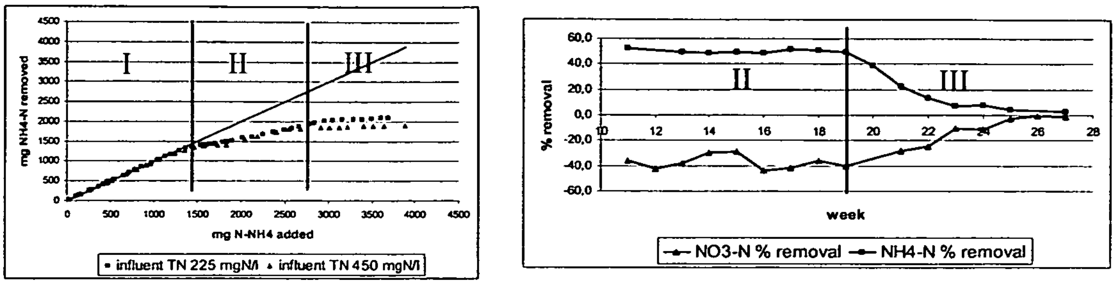

Figure 4. Left: Cumulated mass balance for ammonium nitrogen, mg NH_4^+-N removed against mg NH_4^+-N added per kg non-buffered coco peat; Right: Removal percentages for NH_4^+-N and NO_3^--N during the last 16 weeks for non-buffered coco peat (influent TN 225 mgN/l).

A mass balance showed a reduction percentage for total nitrogen of 29,8% with expanded clay. NH_4^+-N was decreased with 41,5% and NO_3^--N with 19,1%. After approximately 8 weeks of operation, nitrification became evident. Adsorption experiments proved that expanded clay cannot adsorb positive ammonium ions. The negative charged nitrate ion was adsorbed in small quantities: 0,11 mgN/g. The same amount was adsorbed in the presence of phosphate ions.

Lava rock seems to be a very good substrate for nitrification. Almost from the start of the experiments, ammonia was converted to nitrate. From the mass balances for NH_4^+-N and NO_3^--N could be calculated that 93,1% of the NH_4^+-N was nitrified, 5,9% was in solution in the effluent and 1% was present in the capillary water. The average reduction for total nitrogen was 12,5%. During this test period, one column was applied with the same influent but a nitrification inhibitor was added (Allylthiourea). The average reduction for total nitrogen was 40,8%: 29,4% was adsorbed as NH_4^+-N and 11,4% was dissolved as NH_4^+-N and NO_3^--N in capillary water.

CONCLUSIONS

None of the tested lignocellulosic filter media showed an efficient phosphorus removal in these experiments. Removal of total nitrogen was very limited for both peat and coco products. A good nitrification was evident in all the filter media. In non-buffered coco peat a small quantity of nitrate was adsorbed. Because calcium nitrate is used for buffering of coco products, this adsorption will only be present in non-buffered coco products. Of course the overall nitrate removal is negligible. The main mechanism for ammonium removal is nitrification. From a certain point nitrification slows down and consequently ammonium-N removal reduces proportionally.

The light-weight expanded clay produced in Flanders (Argex), shows a good capacity for phosphorus sorption. Taking into account the typical dimensions and characteristics of a vertical subsurface flow constructed wetland (3m²/P.E.; infiltration column 80cm) and the density of Argex, this means the constructed wetland will be saturated after approximately 20 months, assuming 1 P.E. stands for 2 mgP/d. Lava rock seems to be a very good substrate for nitrification. Phosphorus removal is limited but the better than the filter media generally used in constructed wetlands.

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