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Nitrogen removal from industrial wastewater by hybrid constructed wetland systems

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ABSTRACT

The efficiency in nitrogen removal from wastewater generated at CSBP Ltd fertiliser and chemical manufacturer by two hybrid constructed wetland mesocosms was compared. The mesocosms were set up in order to help clarify the reasons why the two year old constructed wetland located at the industrial facility, a 1.2 ha free water surface/vertical flow conjugated system, has performed under the 50% removal expectation (16% for NH_4^+-N, 39% for NO_3^--N and 20% for total nitrogen). It is believed that the short retention time and insufficient oxygen transfer may be limiting nitrification. A free water surface/vertical flow wetland, simulating the design and operation mode of the industry's wetland, and a vertical/horizontal flow, an alternative system, were tested. All systems were set in duplicates and planted with *Schoenoplectus validus*. On average, removals of NH_4^+-N, NO_3^--N and total nitrogen (TN) for the free water surface/vertical flow mesocosm were 79%, 78% and 79% respectively, hydraulic retention time (HRT) was 10.4 days. The vertical/horizontal flow system performed better for ammonium removal (97%) but it failed to remove nitrate properly (-10%), TN removal was 66%, HRT = 8.5 days. The vertical flow stage of the vertical/horizontal flow mesocosm alone removed 95% of the NH_4^+-N and almost doubled the concentration of nitrate in its outflow in 2.4 days, indicating the nitrification capacity of vertical flow systems. The experimental free water surface/vertical flow system which simulates the CSBP wetland outperformed the full scale one and this may be attributed to the lower hydraulic loading rate received by the mesocosm.

Keywords: Constructed wetland, vertical flow, horizontal flow, nitrification, denitrification

INTRODUCTION

Constructed wetlands have been considered as an alternative to conventional wastewater treatment processes due to their moderate capital cost, very low operating and maintenance cost and environmental friendliness (Vymazal, 2005; Kadlec & Knight, 1996). Over the past decade constructed wetlands have been increasingly used for treating a variety of wastewaters including industrial effluents (Green *et al*., 1998; Maine *et al*., 2006).

In 2004 CSBP Ltd, a fertilizer and chemical manufacturer located in Kwinana, Western Australia, built a pilot wetland cell for the treatment of its wastewater. The wastewater produced at different locations within the industrial site mainly consists of cooling tower blow-down water, combined wastewater pumped from production facilities and stormwater runoff. All these wastewater streams are firstly pumped into a containment tank and from there to the constructed wetland. The main concern of the effluent is its high inorganic nitrogen contents, primarily in the form of NH_4^+-N and NO_3^--N, organic waste is not pumped into the wetland as the plant sewerage system uses septic tanks, so the final objective of the wetland is to remove these nitrogen forms.

The wetland is a free water surface/vertical flow conjugated system, approximately 1.2 ha in size and has performed under the 50% removal expectation it was designed for. In order to help clarify the reasons why the wetland has performed below the 50% removal expectation two wetland mesocosms were set up at the Environmental Technology Centre (ETC), Murdoch University. This paper describes the nitrogen removal performance of the pilot wetland at CSBP and the two experimental wetlands at the ETC.

METHODS

CSBP pilot wetland

All wastewater samples were analysed at the CSBP Laboratory. Ammonia was determined as ammonium nitrogen by an ion selective electrode (I.S.E) according to APHA (2005) and nitrate was determined spectrophotometrically according to APHA (1998).

CSBP's pilot constructed wetland characteristics are: 126 m long x 91 m wide x 1 m deep; (~ 1.2 ha) it has a vertical flow design; the medium is sand with a void ratio of approximately 0.3. The influent distribution pipe is laid on the surface of the sediment and the treated effluent drainage pipes are laid underneath the sand column on the surface of the liner, drainage pipes are covered with rocks and geotextile fabric. The wetland vegetation consists of River Club-rush *(Schoenoplectus validus).*

The wetland is operated as a hybrid Free Water Surface/Vertical Flow (FWS/VF) system. The 1m deep sand medium is kept constantly saturated representing the VF and there is a 0.3 m water column on top of the sediment which represents the FWS. The wetland is operated on a fill-stand-drain basis, i.e. after filling to the 0.3 m mark above the sand surface, the wetland holds the water for a few days and is then drained down until the water reaches the surface of the sand. The water that was on the free water component goes to the subsurface component and remains there for a few days. After draining as described above, the wetland is filled up to the 0.3m mark again.

The proposed full scale wetland project would comprise three wetland cells of approximately 1.0 ha each operating in parallel, and receiving an average flow of 2653m^3/day and nitrogen concentrations of the influent would be: NH_4^+-N =22mg//L, NO_3^--N =13 mg/L, TN=35 mg/L. The target nitrogen reduction is 50%.

Experimental wetlands

In order to test the different performances of hybrid systems in removing nitrogen from the wastewater generated at CSBP Kwinana, experimental systems were set up at the Environmental Technology Centre, Murdoch University, Western Australia. A

FWS/VF, simulating CSBP's wetland design was compared to a Vertical Flow/Horizontal Flow (VF/HF) wetland. All system were planted with *Schoenoplectus validus* and set up in duplicates. During the experiment wastewater was brought from the CSBP's containment pond to the location of the experiment every two weeks and stored in the dark at room temperature. Water analyses made by the time of collection at the industry and after it had been stored at location of the experiment for two weeks showed that the concentration of ammonia, nitrate and total nitrogen did not vary significantly.

Once planted, the experimental wetlands were irrigated with scheme water for three weeks and then with the wastewater, this was considered sufficient time to allow for plant and microbial establishment. After this time, sampling started.

Free Water Surface/Vertical Flow hybrid system (FWS/VF)

This set up was meant to simulate in a smaller scale the design and operation mode of CSBP's existing hybrid wetland. For such simulation 200L plastic barrels were used. For the outflow arrangement, PVC perforated pipes were placed on the bottom of the barrels, to avoid clogging, these pipes were covered by a 10 cm layer of gravel (size 1 to 2 cm) and then a 45 cm layer of sand. The depth of the bed was 0.6m. In order to provide a carbon source for denitrification, mulch was placed in one 5 cm layer within the sand column. The sand media was kept totally saturated and the water level was maintained 0.15 m above the sand, the 0.6 m saturated substrate corresponds to the VF system and the water column of 0.15 m represents the FWS system (Figure 1-A). The operation mode of the system followed CSBP's wetland fill and drain operation. On every 6^{th} day the systems were batch loaded with 18 litres of effluent. Before batch loading the system was drained until the water level reached the sand surface, samples were taken at the time of draining. Hydraulic Retention Time (HRT) was designed to be 12 days in total, with the water remaining 6 days in the FWS component and 6 days in the VF component. At the end of the experiment however the system was more heavily loaded and a 6 day total HRT was tested, with the water remaining 3 days in the FWS and 3 days in the VF component.

Vertical Flow/Horizontal Flow hybrid system (VF/HF)

For the VF system the same design of the FWS/VF system was utilised but in this case no wood chips were added and the water level was maintained just below the surface of the sand (Figure 1-B). The system was batch loaded with a volume of 22L/batch. The system was chosen based on the good nitrification capability of VF wetlands (Reed et al., 1995; Cooper, 1999) and it had an air pipe with slots near the bottom end placed vertically through the media which functioned as a passive air pump based on a fill and draw sequence (Green et al., 1997). The HRT for the VF component was initially designed to be 2 days, and the resting period 2 days, but different HRTs and resting times were assessed and compared.

The HF systems consisted of 1.5m x 0.5 m x 0.4m (length x width x depth) tubs. The bottom had a 1.0% slope to assist the water flow through the system. The media chosen was gravel (size 1-2 cm), the depth of the gravel bed was 20 cm. For the inlet a cross sectional pipe with orifices was laid at the proximal end of the tubs (Figure 1-C). For the outflow arrangement, each tub had a collecting PVC perforated pipe placed at its distal end. The HRT for this component was designed to be four days but different HRTs were tested.

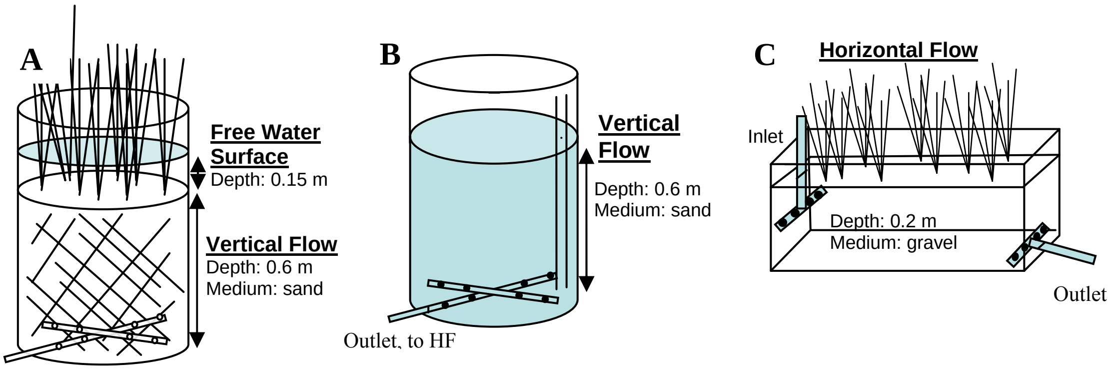

Figure 1: **A**- Free Water Surface/Vertical flow wetland. **B**- Vertical Flow component (plants have been omitted). **C**- Horizontal Flow component.

RESULTS AND DISCUSSION

CSBP pilot wetland

From 09/09/04 to 30/05/06, with the exception of December 2004 and January 2005, due to equipment mal function, the wetland received an average influent volume of 623 m^3/day, which corresponds to a Hydraulic Loading Rate (HLR) of 5.4 cm/day, with average nitrogen concentrations NH_4^+-N= 39 mg/L, NO_3^--N =12 mg/L, TN = 51 mg/L.

Percentage removal in terms of in *vs*. out concentrations for this period was 16%, 39% and 20% for ammonia, nitrate and total nitrogen respectively. Influent and effluent ammonia and nitrate concentrations from September 2004 to May 2006 can be seen in Figure 2 below. TN values although not shown here are the sum of ammonia and nitrate concentrations. It is noticeable that ammonia accounts for most of the nitrogen present in the wastewater and also that in general the influent peaks of ammonia and total nitrogen occur around the winter months which are the rainy months in south Western Australia. This is evidence that the stormwater runoff stream contains substantial amounts of dissolved fertiliser which is washed off the site.

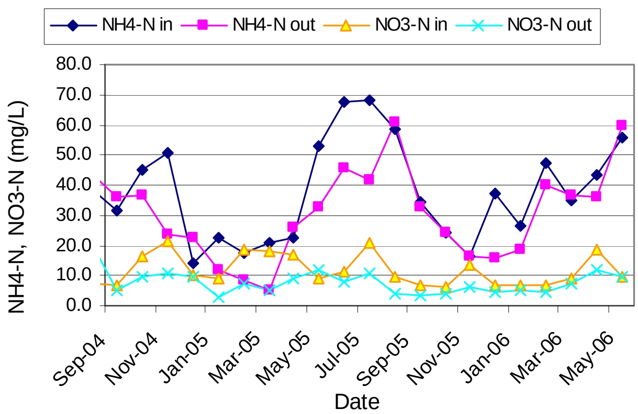

Figure 2: Ammonia and nitrate concentrations measured at the inlet and outlet of the CSBP wetland.

The design and operation of the wetland was guided by the considerations that the oxygen rich free water surface component would allow nitrification to occur, and once infiltrated into the subsurface component and remaining there for a few days, where conditions are anaerobic, this nitrified effluent would be then denitrified.

It is believed that nitrification is limited due to the current operation of the wetland which keeps the substrate totally saturated and means oxygen transfer into the substrate is the main limiting factor for nitrification. Nitrification at the FWS stage requires a longer retention time due to the limited contact with nitrifying biofilms especially when compared to subsurface wetlands. The erratic performance of the wetland can be attributed to the variability in the loading and retention regimes.

Experimental wetlands

The overall average performance of the experimental wetlands can be seen in Table 1 below, sampling started on 26/06/07 and finished on the 12/12/07.

system	rest	HRT	NH_4^+-N in	NH_4^+-N out	removal	NO_3^--N in	NO_3^--N out	removal	TN in	TN out	removal
	days	days	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)
FWS/VF	-	10.4	36.0	7.4	79.4	13.1	2.8	78.4	49.0	10.2	79.1
VF	2.1	2.5	42.3	2.1	94.9	17.4	39.4	-126.4	59.7	42.2	29.3
VF/HF	-	8.5	35.9	1.1	96.9	14.6	16.1	-10.2	50.6	17.3	65.9

Note: FWS/VF: n=48; VF: n=64; VF/HF: n=47. n= number of effluent samples

The FWS/VF wetland which was simulating CSBP's system performed better than the 1.2 ha wetland located at the industry. Removing on average 79.4% of ammonia, 78.4% of nitrate and 79.1% of TN, this higher performance can be mainly attributed to the lower hydraulic loading rate (1.5 cm/day) used in the experiment than that at the CSBP wetland (6.6 cm/day) at the same period. This shows that higher rates of ammonia removal could be achieved at CSBP's wetland with a lower HLR which would result in a longer retention time as demonstrated by the experiment. Another factor could be the smaller size of the experimental wetland which could have a greater positive edge effect on the performance. The influent and effluent concentrations of NH_4^+-N and NO_3^--N are presented in Figure 3. From 09/09/07 on, after approximately 8 weeks of operation, effluent values were low and stable independent of changes in influent concentrations. In the last month of the experiment a 6 day HRT was tested, this new HRT did not affect performance (Figure 3).

The VF component of the VF/HF system efficiently converted ammonia into nitrate, in only one occasion was NH_4^+-N removal below 50%. Nitrate removal was negative in almost all occasions and the overall removal was on average -126%, confirming the effectiveness of nitrification in the VF system operated by batch loading and being fully drained. Nitrate removal was meant to be achieved via denitrification in a subsequent system here represented by the HF bed.

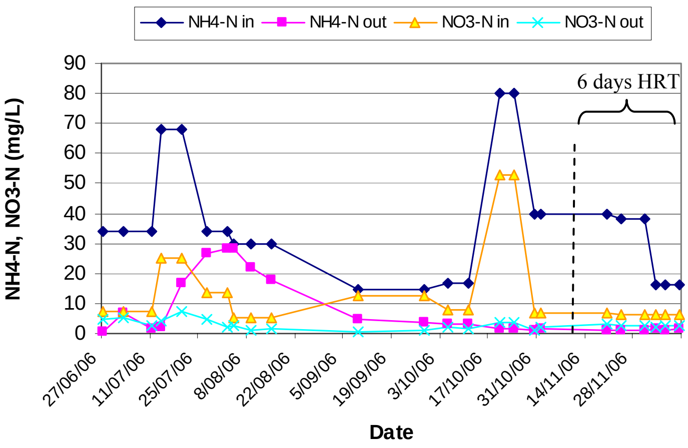

Figure 3: Ammonia and nitrate concentrations measured at the inlet and outlet of the FWS/VF wetland.

The removal of nitrate for the whole VF/HF hybrid system was however unsatisfactory (-10% on average). This is because the HF system further removed ammonia but it was unable to remove the high concentrations of nitrate generated by the VF component (Figure 4). The 0.2 m deep gravel filled HF wetland receiving nitrified effluent failed to remove nitrate as its general conditions were aerobic and it lacked a source of carbon as electron donor to support denitrification (Reed et al., 1995). The addition of wood chips or other plant material should have been considered as an option for a carbon source to help boost denitrification. The average dissolved oxygen (DO) values measured at the outlet of the FWS/VF, VF and HF wetlands and their standard deviations were 0.5 (±0.4); 2.0 (±1.0) and 3.0 (±2.1) mg/L respectively, showing that the HF stage presented the highest DO levels.

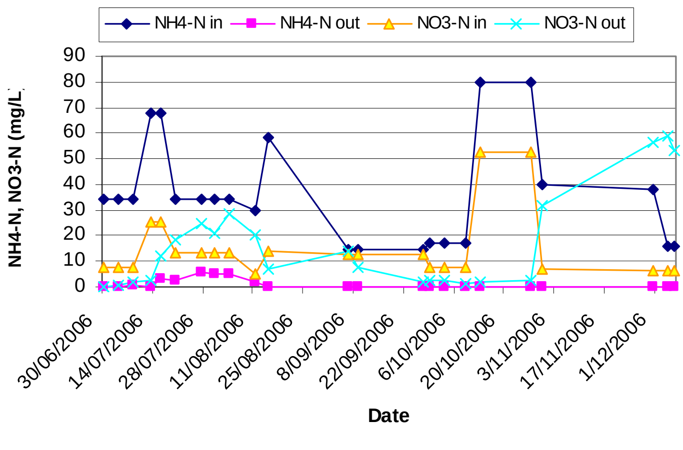

Figure 4: Ammonia and nitrate concentrations measured at the inlet and outlet of the VF/HF hybrid wetland.

From 06/09/2006 on, after approximately 8 weeks of operation the NH_4^+-N effluent concentrations for the VF system were always below 1 mg/L independently of the influent concentrations supporting the theory that the system had reached an equilibrium state in terms of ammonia removal. The NH_4^+-N effluent values for this period were gathered independently, first in regards to the length of the resting time previous to receiving an influent batch (Figure 5-A), and second in regards to the HRT (Figure 5-B). The resting times of 1 day and 2+ days resulted in significantly ($p \leq 0.05$) lower concentrations of effluent ammonia than the resting periods of 0 to 0.5 day, but no difference was found between 1 and 2+ days of resting.

There was no significant difference ($p > 0.05$) in ammonia concentrations among the different HRT tested. These results indicate that the combination of a resting period of 1 day and a HRT of 1 day were enough to produce the lowest concentrations of ammonia in the VF wetlands.

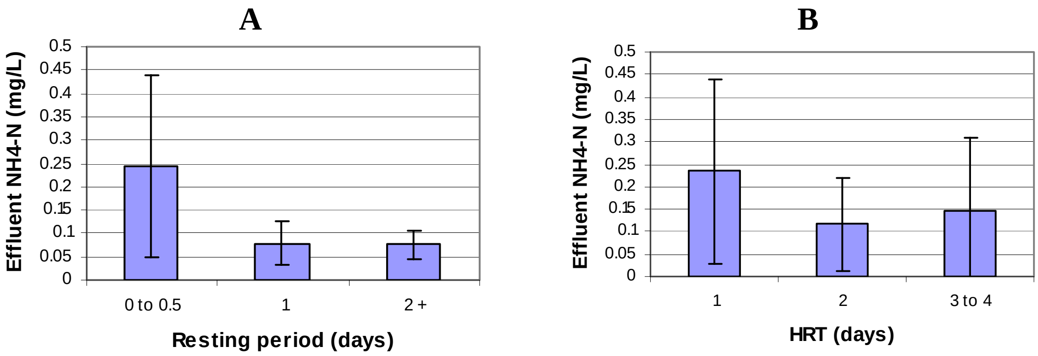

Figure 5: A-VF average ammonia effluent values considering different resting periods. **B**- VF average ammonia effluent values considering different HRT.

The high nitrification capacity of the VF system is in accordance with other VF systems reported in the literature, however while most of the systems are loaded with municipal or domestic wastewater with high BOD, COD (Kayser & Kunst, 2005; Cooper, 1999; Brix & Arias, 2005) this study dealt with inorganic wastewater so all oxygen supplied could be used for nitrification. Results obtained here indicate that shorter resting periods can still produce very low effluent ammonia concentrations with the key factor being the fast draining characteristic of the bed. The fully saturation of the bed during batch is not a problem if fully draining, and therefore re-oxygenation, takes place in between batches.

The FWS/VF hybrid wetland seems to be suitable for nitrate removal given its anaerobic conditions. Ingersoll and Baker (1998) reached nitrate removal efficiencies greater than 90% in FWS microcosm wetlands supplied with a dry plant addition correspondent to 12 kg/m^2/year under HRT of 0.75 day and 1.5 day and temperatures greater than 28ºC. The addition of plant matter (wood chips) in the mid-upper substrate layer of FWS/VF wetlands where sands and influent water lack carbon is a cost effective option to boost denitrification in the early stages when endogenous plant litter is not available.

CONCLUSIONS

The 1.2 ha wetland at CSBP has underperformed in terms of nitrogen removal because it has been overloaded. Ammonia removal in FWS wetlands requires a longer HRT. The potential of the FWS/VF design has been demonstrated by the experimental wetland subject to a lower HLR.

The VF mesocosm has proved to be ideal for removing ammonia from CSBP's inorganic wastewater. The shallow gravel HF wetland failed to remove nitrate. Constructing a deeper HF system would certainly contribute towards keeping the medium anaerobic and favourable for denitrification but due to the cost of gravel this should not be seen as option for the industry.

Based on this study two nitrifying VF wetlands operating in parallel (which would allow for draining and resting), followed by a denitrifying FWS/VF with a carbon input (as per the pilot wetland) have been recommended for CSBP's future wetland expansion plans.

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