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# Effect of External Carbon Sources on Nitrate Removal in Constructed Wetlands Treating Industrial Wastewater: Woodchips and Ethanol Addition

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## Abstract

The present chapter assessed the effect of ethanol and woodchips addition on nitrate removal in free water surface/vertical flow wetland microcosms operated at a 6 day hydraulic retention time, one received increasing ethanol concentrations (COD varying from 58 to 336mg/L) and the other received 2140g (9.3 kg/m$^2$) of dry woodchips. After the addition of COD both system had increased percentage removal of nitrate. COD:$NO_3^-$ ratios applied here with external carbon (16:1 minimum) were higher than the experimental 7:1 reported in the literature for complete denitrification. Excess COD, however, was successfully removed. Parallel to the wetland microcosm, the COD released from woodchips was measured by placing 100g woodchips in 1L of water, COD was measured and the 1L water batch changed weekly. After 65 days the 100g of woodchips released a total of 2262mg COD. These trials were preliminary to a large scale constructed wetland receiving up to 2,000 m$^3$/day of industrial wastewater with high nitrate and low COD. Woodchips, as a low cost biological waste product, can be considered as an alternative to expensive ethanol. Alternatively, the feasibility of using high COD wastewaters from nearby industries is being assessed.

**Keywords**: Denitrification; COD; external carbon source; ethanol; woodchips.

## Introduction

Nitrate nitrogen is an important parameter to be measured in water and wastewater. When released to lakes, rivers and coastal areas it constitutes a main risk for eutrofication and depreciated water quality. In anoxic conditions denitrifying bacteria reduce nitrate to nitrogen gas, this process called denitrification, can be illustrated in a simplified form by equation 1:

$$5C + 4NO_3^- + 2H2O \rightarrow 2N_2 + 4HCO_3^- + CO_2 \qquad (1.0)$$

When nitrogen is present in nitrate form, nitrogen removal via denitrification is generally rapid and complete when organic matter is available; however, denitrification is affected by several parameters, predominantly by a carbon source, anoxic conditions, pH and temperature (Crites and Tchobanoglous, 1998).

Carbon is usually indirectly measured as Chemical Oxygen Demand (COD). The theoretical stoichiometric COD/N ratio calculated by Carrera *et al*. (2003) when using ethanol as C for denitrification was 4.2 g COD : g N. However, experimentally, the COD/N ratio for complete denitrification was found to be 7.1 ± 0.8 g COD : g N. Their experiment showed that there was a loss of about 39% of the COD added which was consumed by oxidation (aerobic respiration) and not by denitrification. Gersberg *et al*. (1983, 1984) also illustrated that the addition of COD should be higher then the theoretical ethanol/nitrogen ratios required for denitrification due to losses of the carbon fraction to aerobic decomposition. When using organic matter such as plant litter or woodchips the resistance to degradation of the lignin fraction must also be observed.

This paper summarises the experimental work performed at the Environmental Technology Centre/Murdoch University (ETC) from September 2007 to January 2008. The work tested ethanol and woodchips as possible carbon sources for a future denitrifying free water surface/vertical flow (FWS/VF) constructed wetland receiving high concentrations of nitrate to be built at CSBP Ltd. CSBP Ltd is a major fertiliser and chemical manufacturer in Western Australia.

## Material and Methods

### *Water Analysis*

Influent and effluent samples were collected and analysed according to the following methods: 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). COD was analysed by the colorimetric determination (potassium dichromate) method with a HACH test kit.

### *COD Release from Woodchips*

To determine the COD ranges of woodchips in water for their potential use as carbon source the following experiments were conducted. 100.0g of dry woodchips was put into a container and filled with 1.0L of tap-water. After storage, between 7 and 15 days, the water was drained and a sample taken. The container was again filled up with 1.0L fresh tap-water. During the 9 week sampling period the trials were run in triplicates. The samples were fixed and stored in the freezer at -15ºC and later analysed. A variation of this experiment was later conducted using CSBP wastewater instead of tap-water, during this second trial shorter retention times were used (4-9 days).

***Experimental Wetland System Description and Operation***

The arrangement of 200L plastic drums is shown in figure 1. Approx. 10cm of medium sized (10-14mm) gravel was placed on the bottom, just enough to cover the outlet pipe to prevent clogging. A 50cm layer of beach sand (porosity 0.3) was used as the main medium for the wetland. The surface was planted with *Schoenoplectus validus*. Once planted the systems were fed with wastewater from mid October to the end of November 2007 to allow bacterial establishment.

*Vertical Flow (VF)* **-** Drums A and C worked as VF wetlands, shown in figure 2. They were batch loaded with 10L of wastewater from CSBP each. Every day the water was drained completely and stored in a separate tank and the wetland was filled up with new wastewater. The intention was to convert nearly all ammonia to nitrate to get higher nitrate concentrations compared to the raw wastewater. Due to evaporation, plant uptake and evapotranspiration the effluent volume was 30% lower than the influent. The effluent from drums A and C is hereafter named A/C blend.

*Free water surface/vertical flow* (FWS/VF) –ethanol and woodchips addition

Drums B, D, E and F were operated as FWS/VF systems (figure 2). Batch loaded with 10L, every 3rd day with A/C blend. The retention time was therefore 6 days, with the water remaining 3 days in the surface and 3 days subsurface. In drums E and F ethanol was added to the influent in different volumes as a carbon source for 5 weeks. Drum D received 2140 g of woodchips as an alternative carbon source. Drum B was found to be faulty and therefore was not used.

Wastewater was pumped from the containment pond at CSBP Ltd, Kwinana into 200L drums, transported and stored at ETC with an average storage time of 14 days. All experimental wetland cells were located at the ETC- Murdoch University.

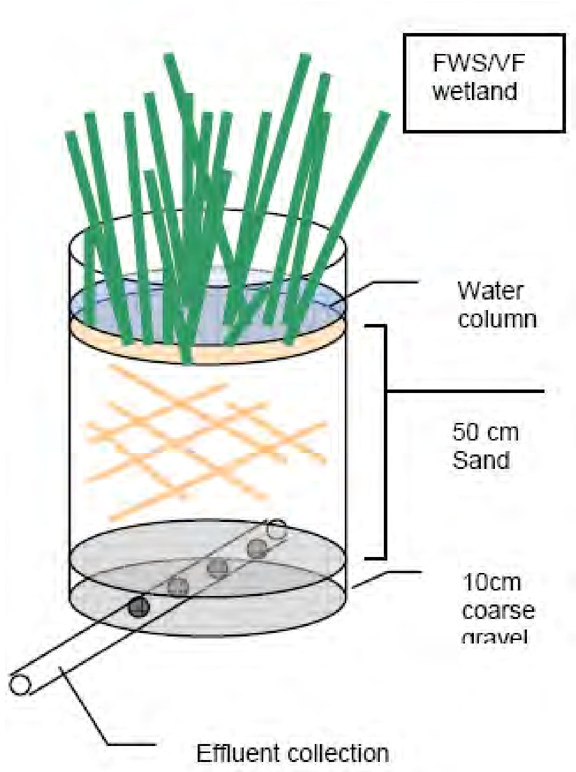

Figure 1. Wetland layout.

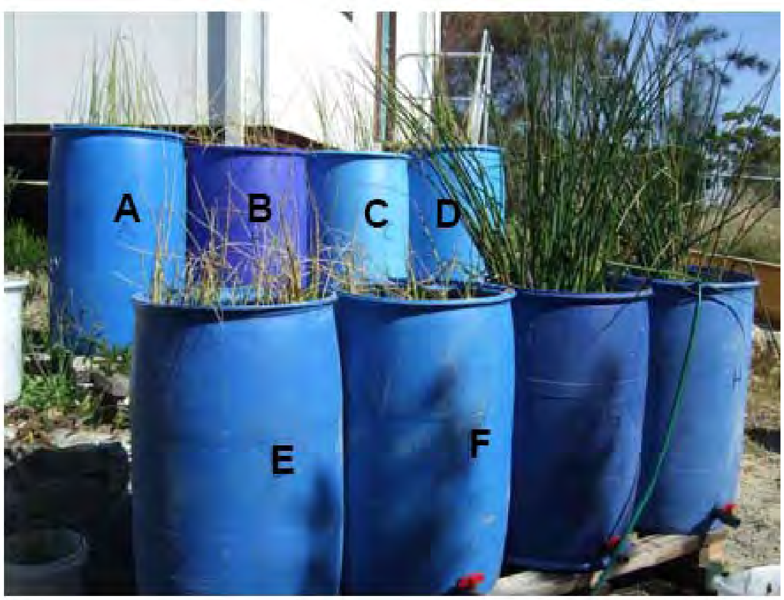

Figure 2. Experimental setup. A,C – VF. D – FWS/VF (woodchips). E,F - FWS/VF (ethanol); B – faulty, not used.

## Results and Discussion

### *COD Release from Woodchips in Water*

After sitting in the water for a week the woodchips turned the water brown. As the water was changed weekly and the woodchips reused this effect became less intense. The results of the COD analysis showed the same trend. With every reuse of the woodchips the level of COD released into the water was lower, starting at 958mg/L (tapwater) and 858 (CSBP wastewater), decreasing very fast over the next few days, and then slower after 40 days of use.

For the tap water experiment, after 50 days the release of COD decreased to levels of 70 - 90 mg/L/week (figure 3). For the CSBP wastewater experiment, after 20 days, the COD released dropped to 205 mg/L. In figure 4 (tap water) the released COD was summed over the time of storage, which makes it possible to calculate the required amount of woodchips for a specific COD level over a certain time. At 65 days a plateau is evident at the cumulative graph (figure 3) with no significant increase of COD taking place. This may be the time to replace the woodchips. This result however should be used just as guidance as COD release will vary depending on the type, coarseness, and age of the woodchips.

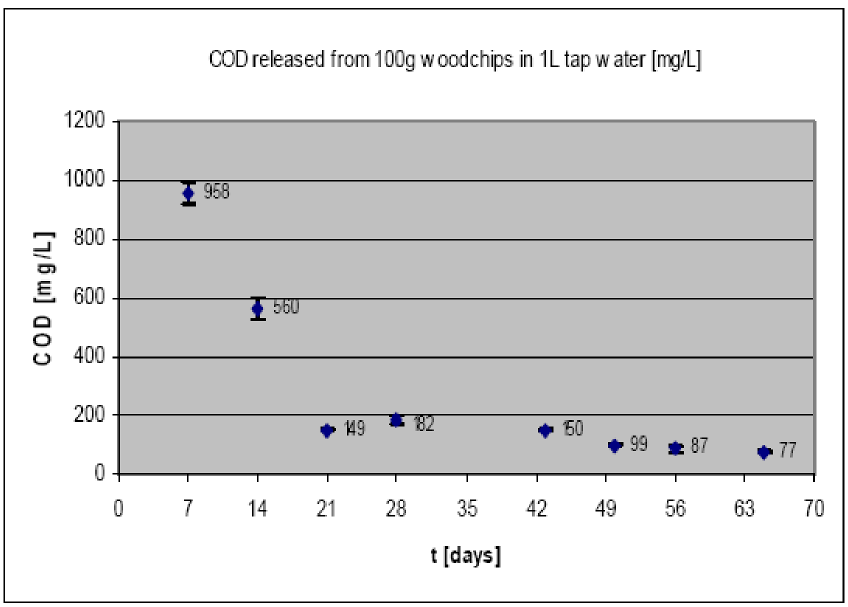


Figure 3. Average COD released from 100g woodchips in 1L tap water over one week intervals. Water exchanged weekly.

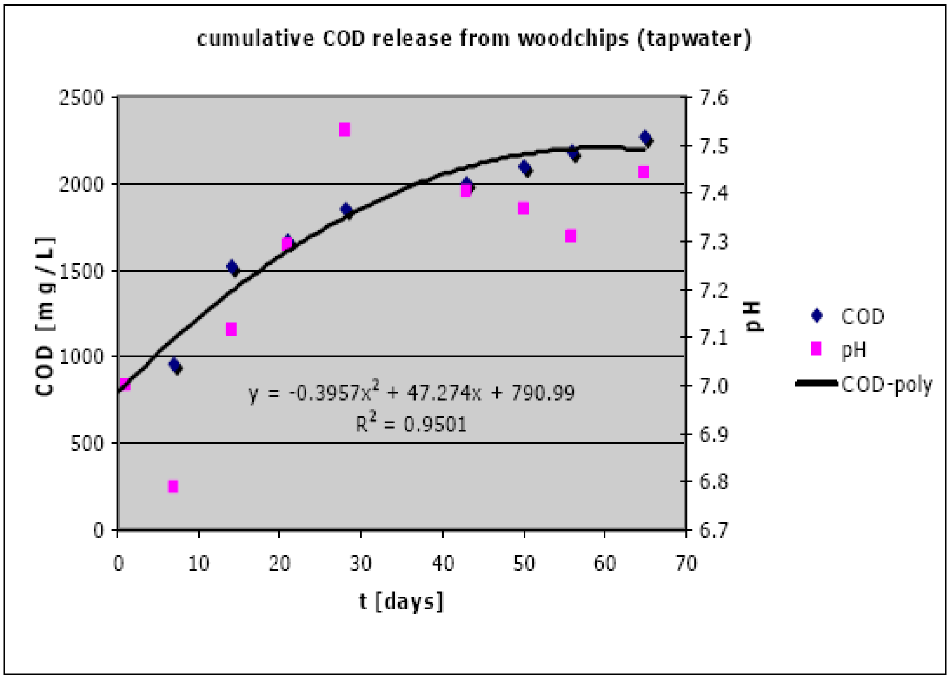


Figure 4. Accumulated COD of 100g woodchips in 1L tap water and pH variation.

For both tap water and wastewater pH decreased to a more acidic level and returned towards neutral again with each sequential reusing of the woodchips. For the wastewater experiment the initial COD of CSBP wastewater (as pumped from the containment pond) was analysed. In order to obtain the COD released from the woodchips, the initial wastewater COD was subtracted from the COD measured after the experiment. The average COD values from 3 CSBP samples were 59.8, 43.8, 49.0 mg/L. Considering the rule of thumb COD:N ratio of 5:1 this would be enough to fully denitrify only up to 11 mg/L nitrate. The experiment showed that woodchips can be used as a slow release COD substrate. A great proportion of COD is released in the first two weeks and then slowly released over the next two months.

***FWS/VF – Nitrate removal - ethanol and woodchips addition***

The performance of the wetlands dosed with ethanol and woodchips are presented in table 1. Due to unexpected nitrate removal by the VF system (low nitrate in the A/C blend), inflow nitrate concentrations were low for the FWS/VF cells before the addition of carbon. Once this problem became apparent, the addition of potassium nitrate into the A/C blend helped increasing nitrate levels in the inflow, alternatively, the use of raw wastewater from CSBP spiked with potassium nitrate also helped.

Table 1. Performance of FWS/VF in removing nitrate when dosed with ethanol or woodchips. Inflow and outflow values shown are means ± standard deviation.

| | Cells E + F | | | Cell D | |
|---|---|---|---|---|---|
| | Before ethanol | Ethanol (cycle 4-8) | Ethanol (cycle 9-12) | Before woodchips | Woodchips |
| Inflow $NO_3$-N[mg/L] | 2.0±0.4 | 10.9±1.1 | 20.9±2.6 | 2.0±0.4 | 14.8±2.8 |
| Outflow$NO_3$-N [mg/L] | 1.1±0.2 | 1.9±0.4 | 2.0±0.2 | 1.4±0.17 | 2.3±0.3 |
| Removal [%] | 46 | 82 | 90 | 31 | 84 |
| Inflow COD [mg/L] | - | 247 | 336 | - | 1800-400 * |
| COD:$NO_3$-N | - | 22:1 | 16:1 | - | ≥27:1 * |

* Estimated based on the COD release, woodchip experiment.

*Ethanol*- Before ethanol addition nitrate removal was in the order of 46%. After adding ethanol to the system nitrate removal steadily increased reaching 90% removal by the end of the experiment. Because of improper mixing of the ethanol with the wastewater and erroneous sampling method used during the first cycles (1-3) the results obtained from this period are biased and must not be considered. For cycles 4-8 and 9-12 the mixing and sampling methods were corrected. During cycles 4-8 the average inflow COD:$NO_3^-$ ratio was 22:1, this resulted in approximately 82% nitrate removal. The following cycles (9 -12) had a lower COD:$NO_3^-$ ratio of 16:1, however, nitrate removal increased to 90%. This is contrary to what was expected as a higher COD: $NO_3^-$ ratio generally results in a higher nitrate removal. In terms of outflow nitrate concentration there was no difference between the two sets of trials. A few ideas arose from these results:

- COD: $NO_3^-$ ratios higher than 7:1 (literature) did not affect denitrification;
- Outflow nitrate concentrations of 1 to 2 mg/L could be expected as a background level for FWS/VF wetlands, even when the system is performing best;
- System maturation may also have contributed to improved treatment performance.

Nitrate influent and effluent values can be seen in figure 5. Increased inflow and outflow nitrate concentrations towards the end of the experiment are noticeable.

*Woodchips*- Wetland cell D had on average 31% nitrate removal before the addition of COD in the form of woodchips. The addition of 2140g of woodchips increased removal to 84%. In terms of mass/area the application of woodchips was 9.3 kg/m$^2$. The influent COD was measured, but the amount of COD released by the woodchips within the wetland could just be estimated based on the previous experiment. When compared to the woodchip experiment mentioned earlier the quantity applied here (214g/L – from 2140g and 10L batches) is twice as much as the one used in the experiment (100g/L). The experiment showed that after 23 days under water and 6 day retention time the COD released to the wastewater was 205 mg/L. We could expect approximately twice as much COD being released in the water from each batch at cell D (~400mg/L after 23 days). It has been estimated that from the day woodchips were placed in cell D, COD:$NO_3^-$ ratio was maintained at a minimum of 27:1.

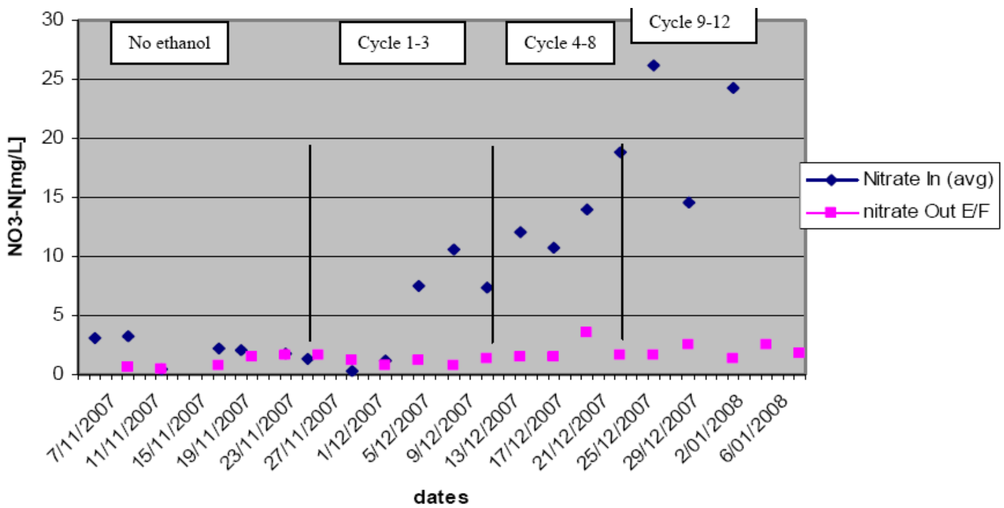


Figure 5. Nitrate removal in FWS/VF cells E/F where ethanol was added.

Inflow and outflow nitrate concentrations for wetland cell D can be seen in figure 6, influent nitrate concentrations were raised concomitantly when woodchips were introduced, outflow nitrate levels however remained low, although there was more COD available outflow nitrate could not be lowered below 1.4 mg/L. Nitrate removal increased after the addition of woodchips and ethanol into the systems. In both cases COD: $NO_3^-$ ratios were maintained at levels higher than those previously reported in the literature. In terms of final effluent quality the addition of an external carbon source did not play a role in decreasing nitrate concentrations beyond the 1 and 2 mg/L values. These effluent concentrations were also achieved without carbon, but in the period before carbon was added nitrate influent values were always low and never above 8 mg/L.

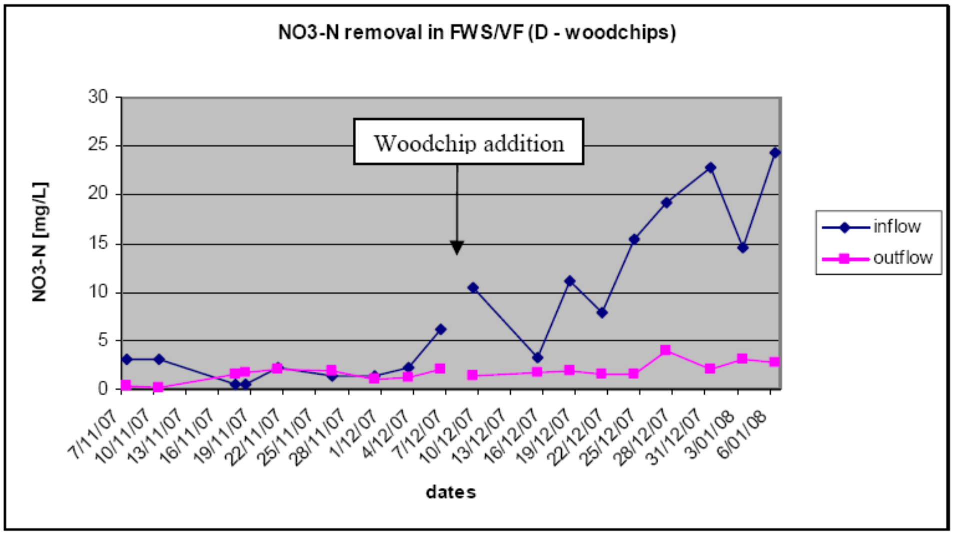


Figure 6. Nitrate removal in FWS/VF where woodchips were added.

The consumption of carbon in cells E+F brought COD values closer to the COD of CSBP wastewater (as pumped from containment pond) (figure 7). The same pattern was observed for cell D, the effluent COD after woodchip addition was on average 76.6mg/L (±11) while the influent COD of CSBP wastewater for the same period was 58.7mg/L (±17). The experiments showed that COD was successfully removed within the FWS/VF wetlands, nonetheless, final effluent COD from the future denitrifying wetland cells is an important parameter to be measured as it should not vary much from the actual COD values of the effluent being discharged, otherwise, COD discharge regulation/license will need to be reviewed. In many wastewater treatment systems the rule of thumb for the COD:N ratio is 5:1 at the denitrifying stage. Table 2 shows different carbon sources used in various denitrification studies.

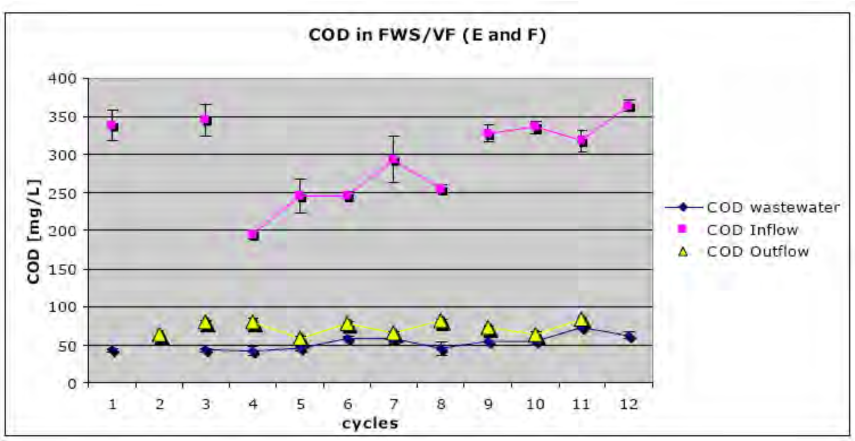


Figure 7. COD in FWS/VF cells E/F dosed with ethanol.

Table 2. Different carbon sources, C:N ratios and nitrate removal reported in various studies.

| Reference | Carbon source | Ratios | $NO_3^-$ - N influent concentration | $NO_3^-$ - N removal |
|---|---|---|---|---|
| Davidsson and Stahl (2000) | Organic Matter (organic soils) Glucose | C : N = 6.6 : 1 | 200μM $KNO_3$ | ≤73% |
| Ingersoll and Baker (1998) | Organic Matter (chopped cattails) | C:N= 5:1 (C : NO3-N) | 30mg/L | >80% |
| Constantin and Fick (1997) | Ethanol Acetic acid | C:N = 1.38 : 1 1.46 : 1 (mol : mol) | 7.1g /L | - |
| Carrera et al. (2003) | Ethanol | COD: N mass ratio 4.2:1 (stoichiometric) 7.1 ± 0.8 : 1 (experimental) | - | - |
| McAdam and Judd (2007) | Ethanol | C: N mass ratio < 1.52 : 1 | 14.7mg/L | 92% |
| Gabaldon et al. (2007) | Methanol | COD:NO3-N mass ratio 3.31:1 | 140-210 mg/L | >90% |
| Lin et al. (2002) | Macrophytes and Fructose | COD:NO3-N mass ratio ≤6.2:1 | 21 -47mg/L | >90% |

## Conclusion and Future Studies

Although preliminary this research showed that:

- Nitrate removal increased when ethanol and woodchips were added to the wetlands.
- Both ethanol and woodchips are suitable carbon sources for enhancing denitrification in FWS/VF wetlands.
- Woodchips (100g/L) released COD in sufficient quantity to support denitrification for at least two months in a FWS/VF system.
- Excess COD was successfully removed by the FWS/VF wetlands.
- The COD:$NO_3^-$-N ratio of 7:1 suggested by the literature should be followed for the future carbon dosing of theFWS/VF wetland cell at CSBP.
- Even at the best performance final nitrate concentrations of 1.0 – 3.0mg/L can be expected for future FWS/VF wetlands at CSBP (HRT = 6 days) considering a 7:1 minimum COD:$NO_3^-$-N ratio.

Because the control (without external carbon) and treatment (with carbon) conditions did not occur simultaneously but consecutively, under different environmental conditions and subject to much lower influent nitrate concentrations when the carbon source was not present, the effect of the carbon source on the performance of the systems is just an indication. Comparisons between the periods prior to carbon addition and after carbon addition should be made only very carefully due to this experimental limitation. Further studies on low cost carbon sources for denitrification such as wastewater from a local soft-drink industry are being conducted under an improved experimental design where the control and treatment wetlands run in parallel subject to the same conditions and influent nitrate concentrations.

## Acknowledgements

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