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# **The denitrification efficiency of the new effluent in zin conference**

## **centre constructed wetland**

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#### **Abstract**

Wetland is a natural system of water treatment. It has been used as waste water treatment system in many countries in Europe. The vertical flow constructed wetland of different water level are efficient in removing Nutrients, TSS, heavy metals and toxic compounds from waste water. Nutrients are effectively removed from domestic wastes through microbial nitrification-denitrification path way. Excess nitrogen in water bodies are the major causes of Eutrophication. The aim of this study is to optimize the nitrogen removal efficiency of vertical flow wetland using different water levels from Zin conference centre wetlands. The samples were collected from influents and two effluents- old and new for COD, BOD,  $NH_4-N$ ,  $NO_3-N$ , TKN and TN analysis. The data were analyzed using SPSS to see the significance between factors. Results showed that the average NO3-N in the effluent is 0,17**+** 0,23 mg/L but in the old and new effluents are 55**+**12,3 mg/L and 46,5**+**12,7 mg/L respectively. The NH4-N concentration was significantly decreased from influent 62,8 **+** 17 mg/L to effluents 0,21**+** 0,2 mg/L and 2,75**+** 4,6 mg/L in the old and new effluents respectively. The COD concentration was significantly decrease from 379**+**130 mg/L in the influent to 38**+**11,7 mg/L and 35,3**+**22,0 mg/L in the old and new effluent respectively. The shortage of COD in the effluent affects the denitrification and nitrification processes in the wetland.

**Keywords:** Key words: Domestic wastewater, Microbial Nitrification-denitrification, Water levels, Nitrogen removal efficiency, Eutrophication.

#### **1. Introduction**

A "constructed wetland" is a wetland specifically constructed for the purpose of pollution control and waste management, at a location other than existing natural wetlands (EPA, 1993). CWs remove nitrogen from waste water through two pathways: Storage (assimilation or adsorption) in the system, and removal through denitrification and ammonia volatilization (Donald, 1990). Optimization of denitrification reliability and efficiency will help to ensure that constructed wetlands are an economically feasible treatment technology.

The first experiments using wetland macrophytes for wastewater treatment were carried out in Germany in the early 1950s. Since then, the constructed wetlands have evolved into a reliable wastewater treatment technology for various types of wastewater.

Wastewater treatment for removal of Nitrogen is important because nitrogen compounds are the major pollutants that create a potential hazard to living things and the ecosystem. High nitrogen concentrations in water can directly affect human health, as when nitrate in drinking water causes methemoglobinemia in infants, commonly known as 'blue baby syndrome' (Crites and Tchobanoglous 1998). However, the primary impact of nitrogen is due to its role as a limiting nutrient in many aquatic environments. Elevated nitrogen inputs in water bodies can cause eutrophication. Eutrophication due to nitrogen inputs have been implicated in loss of species diversity (Preston et al. 2003) and increased occurrence of harmful algal blooms such as red tide, which threaten both human and ecosystem health (Anderson et al. 2002, Huang et al. 2003). Excessive nutrients in aquatic systems lead to decreased dissolved oxygen levels and fish kills (Cook, 2001).



Nitrogen is main nutrient found in wastewater in high quantities. Nitrogen is mostly found in the form of nitrates in the water. Some of the problems associated with high levels of nitrates in drinking water or surface water are: serious health effects in humans and eutrophication in lakes and ponds. Wastewater from agriculture and sewage contains high levels of these nutrients and constructed treatment wetlands are capable of reducing their levels.

The process of nitrogen removal by bacterial conversions in wetlands follows a series of reactions. The nitrogen cycle has 3 main processes. Ammonification which is the conversion of organic N to NH4+. The second process is nitrification which is a two step process – conversion of NH4+ to Nitrite and conversion of nitrite to nitrate. The third process is denitrification – where nitrates convert to nitrites and conversion of nitrites to organic N.



**Figure 1. Simplified nitrogen cycle** (Nitrogen cycles project)

## **2. Material and methods**

## **2.1 Study area**

ZIN is an area located in the southern part of the Netherlands. Its particular location is 51038'19.20"Nand 5018'22.07"E. Previously it was a monastery. In 2000 it was converted into a conference building. Currently, the place is known by the name ZIN conference center (ZCC). There are more than 10 hectares of land surrounding ZCC. The majority of the land (nearly 7.5 hectares) is used for garden. The irrigated land consumes about 13m3 of water per day (Shrestha, 2007). The monk quarter, workshop and the main conference building are the sources of the wastewater in ZIN.

In ZIN a kidney shaped constructed-wetland (CW) was built for the first time in 2000 to treat the wastewater generated from the three buildings. The wetland was very efficient in treating the incoming wastewater. Because of the increased number of customers and workers of the ZCC and the ease of the wetland in treating wastewater, an additional new vertical flow –constructed wetland (VF-CW) which is similar to the old one was built in 2004 near the existing wetlands to treat the extra wastewater produced. The arrangement of the CWs and the buildings are demonstrated by the following schematic drawing





Figure 2: Schematic drawing of ZCC wetlands (Source: Shrestha, 2007)

The existing design parameters of the constructed wetlands were carefully studied. The wetlands were designed according to population equivalent (PE). One person has the ability to produce 120 to 150L of wastewater per day (Shrestha, 2007). Thus, the wetlands were designed on the basis of 3.5m2/PE. Design flow rate is 3.5m3/day. The bed area of the wetland is 95m2. Phragmite is the microphite covering the two wetlands.

The filter media which have 40% porosity were arranged in different layers (FIGURE 3).



Figure 3: A schematic drawing for the cross section of the ZCC-CW

#### **2.2 Water sampling**

There were three sampling place in ZIN wetlands. Samples were collected from influent and effluent. They were collected and transported at the same day using a cool box containing ice cube. The sampling dates were 17-9-2009, 10-10-2009, 19-11- 2009, 31-12-2009 and 27-02-2010.

## **2.3 Analytical methods and equipments**

A brief description of the methods and equipments used to measure parameters of concern for this research work is presented in the following sub sections. Chemical analyses were performed following the methods described in Environmental chemistry (Kruis, 2005). Temperature, conductivity, pH, NH4+-N, TN, NO3--N, COD, BOD and TKN were monitored. For each of the parameters, samples were analyzed in duplicates in order to minimize errors. The samples were only filtered for ammonium and nitrate analyses.

#### **2.6 Data analysis**

To determine whether the treatment performances of the wetland statistically one-way ANOVA and t-test at a significance level of 0.05 was used. These analyses were conducted by using a sub-program of Microsoft Office Software EXCEL XP. The statistical results were reported as: for t-test result as (t-value, df and p-values) and for ANOVA result as (One-way ANOVA;F0.95 (d.f.:dN); p) where  $F0.95 = 95n$  % confidence limit; d.f.: degree of freedom;  $dN =$  sample size;  $p > 0.05$  non significance in the related section of result and discussions.

## **3. Results and Discussion**

The characteristics of the domestic wastewater added to the constructed wetlands in some countries have been summarized from the literature and are presented in Table 2 to compare with ZIN wastewater.

The BOD5 value of the ZCC wastewater  $(217.8 + 33.2 \text{ mgl-1})$  is nearly the same as the typical BOD5 value of raw domestic water (220 mgL-1). In addition, the COD: BOD5 ratio of ZCC is 1.74, which is slightly higher than that of the typical value of 1.14 mgL-1 (Vymazal et al., 1998) is similar to German wastewater. Thus, it can be conclude that the domestic wastewater of ZCC is low biodegradable comparing to the typical domestic wastewater but comparing to other countries is more degradable. The reason for this could be the workshop in the ZCC is releasing non-degradable waste to the treatment wetlands. COD, ammonium and TN content of the domestic wastewater of ZCC has close similarity with German domestic wastewater as cited by (Vymazal et al, 1998).

References	Parameters $(mg/L)$							
	<b>BOD</b> 5	$\rm COD$	COD: BOD <sub>5</sub>	<b>TSS</b>	<b>TP</b>	$NH4+N$	$NO3-N$	<b>TN</b>
Germany1	248	430	1.73		15.9	80.50	1.90	115
France1	215	495	2.30	225	8.50	25.00	2.85	46.0
Nepal <sub>2</sub>	110	325	2.95	83.0		33.00	$\overline{\phantom{a}}$	
Poland <sub>3</sub>	110	283	2.57	140	7.65		$\overline{\phantom{0}}$	46.1
Slovenia3	107	200	1.87	$\overline{\phantom{a}}$		28.70	$\overline{\phantom{a}}$	
Germany-Bavaria3	106	234	2.21				$\overline{\phantom{0}}$	
Denmark and UK3	97	264	2.72	98.6	8.60	21.00	$\overline{\phantom{a}}$	36.6
Czech Republic3	87.2	211	2.42	64.8	6.57	28.10	$\blacksquare$	46.4

Table 2: Characteristics of the domestic wastewater applied to the Constructed Wetlands.



(Source: Korkusuz, 2002)

References: 1Vymazal et al., 1998; 2Shreshta et al., 2000; 3Vymazal et al., 2000; 4 Tchobanoglous and Burton, 19

#### **Temperature, pH, Dissolved Oxygen and Conductivity**





(Where Inf= influents, Eff O = effluent old and Eff  $N =$  effluent new)

The wastewater entering the wetlands had higher temperature as compared to that of effluents. Mean temperature of the influent was 13.40c which was higher than the effluents 8.50C and 8.20C (new and old) respectively. The temperature in the influent is higher than in the effluents because the influent wastewater came from the kitchen and the bathroom.

As the wastewater passed through the wetland, the pH in the effluent became smaller than the influent. The pH changed from 7.4 in the influent to the 6.3 and 6.7 in the old and new effluents respectively. The main reason for the reduction of the pH value is the prevailing of nitrification in the wetlands (Shrestha, 2007).

There are plant root zone oxygen releases to the wetlands. Different researchers indicated different values for oxygen transfer in wetlands; (Brix et al., 1996) reported that the oxygen transfer by plants is 20mg O2 / m2.d. But (Gries et al., 1990 and Armstrong et al., 1990) reported that the plant oxygen transfer has a range from 2 to 12g O2 / m2.d. Intermittent feeding is also another reason for the increase in oxygen content inside the wetlands. The above reasons made the wetlands to have the oxygen content in the effluent higher than in the influent. Dissolved oxygen (DO) increased from 0.8mg/L in the influent to 6.6 and 1.1mg/L in the old and new effluents respectively.

The mean electrical conductivity (EC) of the influent and effluents were also recorded during the monitoring periods. The EC at the influent was 1369 µS/cm. The conductivity was the same throughout the measured samples. The EC in the new effluent was very low in comparison to the old effluent. The raising the water level of the new effluent increases the retention time of the effluent as a result the some ions were removed by sedimentation and adsorption of the ions with the particles in the wetlands.

#### **Nitrogen**

Nitrogen in wastewater exists commonly in the form of ammonia, organic, nitrate, nitrite, and gaseous nitrogen. All these forms of nitrogen are biochemically inter-convertible and are components of nitrogen cycle. Nitrogen compounds, especially ammonia, can exert a significant oxygen demand through biological nitrification; may cause eutrophication in receiving waters; and can be toxic to aquatic organisms.

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Parameters	Influent			Effluent-old			Effluent-new		
	Min	max	$Mean + Stdev$	Min	max	$Mean + Stdev$	Min	max	Mean+ stdev
$NO3-N$	0,02	0,53	$0,17+0,23$	44	71	$55+12.3$	36	93,6	$46,5+12,7$
<b>BOD</b>	80	245	$190.2 + 68$	$\overline{4}$	9	$6.8 + 2.1$	$\overline{4}$	4.6	$4.5 + 0.6$
NH4-N	43	87,3	$62.8 + 17$	0.1	0.5	$0,21+0,2$	0.1	9,6	$2,75+4,6$
<b>TKN</b>	49.5	97,2	$76,6+18,3$	0.6	3	$1,6+1,1$	0.5	10,5	$3,7+4,6$
TN	49.5	97,5	$76.9 + 18.5$	47	71,6	$56,6+11$	43.9	94,5	$50,2+10,1$
<b>COD</b>	211	581	$379+130$	29	55	$38 + 11,7$	10	50	$35,3+22,0$

Table 4: Influent and effluent concentrations of ZIN, in mg/L

The results of the different forms of nitrogen during the monitoring period were presented graphically in Figure 5(A to D). In this figure, time versus influent and effluent concentrations (with their standard deviations) for, COD, NH<sub>4</sub>-N, NO<sub>3</sub>-N, and TN is indicated. The minimum and maximum concentrations of the influents are also given in table 4.





Figure 5: time Vs concentration; A. Ammonia, B. Nitrite, C. Nitrate & D. TKN

### **Ammonium Nitrogen**

In recent years, constructed wetlands have also been used extensively for tertiary treatment (IWA, 2000). Nitrogen can be removed from constructed wetlands through volatilization, ammonification, nitrification/denitrification, plant uptake and matrix adsorption. Latest studies have verified that the major removal mechanism in most of the constructed wetlands is microbial nitrification/denitrification (Vymazal et al., 1998). However, (IWA, 2000) proved that nitrogen removal performance of vertical flow wetlands treating ammonium-rich wastewater is often relatively poor.

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At higher loads to the wetlands, only suspended solid and carbon removal can be very important (Vymazal et al., 1998). Whereas, at lower loads nitrification and denitrification can take place, in order to have efficient

nitrification, most of the biodegradable carbon has to be removed first from the wastewater, enabling the nitrifying bacteria to convert ammonium to nitrate (Korkusuz et al., 2004). In intermittently loaded vertical flow system wetlands, nitrification processes increased in several folds because it facilitates oxygen transfer rate in the wetland matrix. The nitrate produced can subsequently be reduced to nitrogen gas by biological denitrification if there is readily available carbon source (Vymazal et al, 1998)



Figure 6:  $\text{COD:BOD}_5$  ratio concentration vs. time in ZIN

In ZIN, the NH4-N effluent concentrations of the old wetland (Figure 5A) varied between 0.1 and 0.5 mg/L with an average  $0.21 + 0.2$  mg/L while the new effluent varied between 0.1 and 9.6 mg/L with an average of 2.75 + 4.6 mg/L. The concentration- based NH4+-N removal efficiencies of the ZIN old wetland varied between 99.18 and 99.89 % (99, 72 + 0.31%), whereas in the new effluent varied between 87.2 and 99.43%  $(95.75 + 6.22%)$ . Even though the ammonium removal performance of the old effluent wetland seems to be a little bit better than the new effluent wetland, statistically the two effluents are good in removing ammonium from the wastewater. Therefore, according to the t-test statistical result there is no significant difference between the old and the new effluents ( $t = -1.697$ ,  $df = 8$  and  $P = 0.128$ ).

The higher nitrification capacity of the intermittently operated vertical flow wetlands can be attributed to enhanced oxygen transfer from the atmosphere to the beds (Brix, 1997). The lower biodegerability of the ZIN wastewater applied to the wetlands (table 3), the available oxygen in the cells might have been used for nitrification instead of carbon removal (Korkusuz, 2004). Moreover, the matured Phragmites in ZIN wetlands might have slightly increased nitrification through oxygenation of the substrate. (Shrestha, 2007) reported that



the removal efficiency of the wetlands for ammonium was 88%. From this we can conclude that there is no problem of nitrification in both of wetlands in the ZIN. Nitrification of ammonium has successfully taken place in ZIN wetlands.



Figure 7: NH<sub>4</sub>-N loading rate ( $g/m^2$ .d) vs. removal rate ( $g/m^2$ .d) at CWs of ZIN.

Ammonium loading rate in old and new wetlands varied between 1.58 to 3.21  $g/m2$ .d (2.4 + 0.66  $g/m2$ .d) and 1.56 to 3.2 g/m2.d (2.32 to 0.69 g/m2.d) respectively. As a rule there is no linear relation between effluent concentration and loading rate of NH4-N. But the existing situation in ZIN makes to have strong correlation between loading and removal rates, R2=0.9401 and R2=0.9998 respectively.

## **Nitrate –Nitrogen**

The mean influent nitrate concentration of ZIN was  $0.17 + 0.23$  mg/L and the rang is between 0.02 to 0.53 mg/L. When the wastewater was passed via the system, NH4-N was oxidized to NO3-N and the average NO3- N was increased to 55 + 12.3 mg/L and 46.5 + 12.7 mg/L in the old and new effluents consecutively. (Shrestha, 2007) reported that the NO3-N concentration of the new effluent was  $71 + 12$  mg/L which is higher than this study  $46.5 + 12.7$  mg/L. The decrease in concentration is due to the conversion of nitrate by denitrification. Thus, the increase in the depth of the new effluent has an affirmative effect in nitrogen removal. In order to have efficient nitrogen removal, most of the biodegradable carbon has first to be removed from the wastewater, enabling the nitrifying bacteria to convert ammonium to nitrate easily (Haberl et al., 1995). The independent sample t-test value indicated that there is no significant difference between the old and the new effluents in removing nitrate from the wastewater entering the treatment wetlands at ZIN ( $t = 0.155$ ,  $df = 8$  and  $P = 0.881$ ).

The BOD5 of the wastewater must be less than 20 mg/L before significant nitrification can occur (Reed, et al., 1995). Temperature and water retention time in the wetland are also an important factor for the rate of nitrification. Temperatures below 15 0C can significantly reduce nitrification (Reddy and Patrick, 1984). Nitrification can readily occur down to 0.3mg/L dissolved oxygen. The BOD5 and DO of the system are in a favorable condition for nitrification to occur. But temperature in the wetland was very less. So, the main reason for the reduction of nitrate to  $(55.9 + 23.8 \text{ mg/L})$  from Shrestha's result  $(71 + 12 \text{ mg/L})$  is due to the establishment of denitrification zone within the wetland as a result of raising the effluent by one meter higher.

In the wetland system under investigation,  $NO_3-N$  production vs.  $NH_4-N$  loading rate for both old and new effluents was plotted. The regressions of the points  $R^2 = 0.074$  for the old and  $R^2 = 0.079$  for new showed that there is linear relationship between the two wetlands. As NH4-N loading rate increased the production of NO3- N in the two wetlands decreased (figure 5 A and C). The decreasing in  $NO<sub>3</sub>-N$  concentration is an indicator that some of the nitrates were converted to nitrogen gas by denitrifying bacteria.



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Figure 8: NH<sub>4</sub>-N loading rate (g/m<sup>2</sup>.d) Vs. NO<sub>3</sub>-N effluent concentration (mg/L) and NH<sub>4</sub>-N loading rate (g/m<sup>2</sup>.d)

vs. NO<sub>3</sub>-N production rate  $(g/m^2.d)$ 

The correlation between ammonium loading rate and nitrate production was very small for both new and old effluents,  $R2=0.2381$  and  $R2=0.011$  respectively. In the new effluent, as the ammonium loading rate increased the nitrate production wasn't change. This indicates the availability of oxygen was very low in the higher water level. But in the old effluent the nitrate production increases with ammonium loading rate comparing to the new effluents. In the old effluent, nitrate production increases with increasing ammonium loading rates. Figure 5C, depicted that there is no significance difference in the nitrification rate between the old and the new effluent as  $p > 0.05$ .

## **Total Nitrogen (TN)**

The TN in the effluent is the summation of TKN  $(NH_4-N)$  and organic nitrogen), inorganic Nitrates  $(NO_2-N)$ and Nitrites (NO3-N). Nitrogen was also eliminated from the wetlands via dentrification, volatilizationand sedimentation.

	Minimum	Maximum	$Mean + stdev$	Removal efficiency,%
TN in Influent	49.5	97.5	$76.9 + 18.5$	$\overline{\phantom{0}}$
TN Effluent old	$4^{\circ}$	71,6	$56,6+11,3$	$24,3 + 15,6$
TN Effluent New	43,9	94,5	$50,2 + 10,1$	$32,3 + 17$

Table 5: The TN and its removal efficiency of old and new effluents of ZIN

The TN removal efficiency in CWs at ZIN ranges from 5.08 to  $40.27\%$  (24.3 + 15.58%) for the old wetland and 3.08 to 48.8 %  $(32.3 + 17.1%)$  for the new wetland (table 5). The new effluent wetland has greater removal efficiency comparing to the old effluent. All conditions in the old and the new effluents were the same except the new effluent raise the water level to 1m higher than the old effluent. The existing condition found in the new wetland was denitrification. From the result of the activity measurement, the new wetland has high denitrification potential than the old one. But the denitrification activity was inhibited by shortage of carbon sources.

Both wetlands have very near efficiency in removing nitrogen. According to the independent sample t-test result ( $t = 0.013$ ,  $df = 8$  and  $P = 0.99$ ) there was no significance difference between the old and the new effluent wetlands in removing total nitrogen. But figure 10 showed that there was a difference of 7.9 mg/L in TN between the old and the new wetlands.





Figure 9: TN removal efficiency of the old and new effluents of ZIN

## **4.** Co**nclusion**

The study focused on the potential use of Vertical Flow Constructed Wetlands in removing nitrogen from domestic wastewater at different water levels. It demonstrates that the aerobic and anaerobic conditions are important focus in removing nitrogen from domestic wastewater in the treatment wetlands.

The findings of this research showed that there was a significance difference between water levels in removing nitrogen from wetlands. New effluent at higher water level in ZIN wetland has higher removal efficiency for TN, BOD and COD than the old effluent wetland. TN removal in ZIN (Old and New) effluent was 32.3% and 24.3% respectively. And COD removal in ZIN new and old effluents was 94.6% and 89.3% respectively. Nitrate production in the new effluent wetland (46.5 mg/L) was lower than in the old effluent (55 mg/L) because in the new effluent wetland anaerobic condition was created as a result of raising the water level of the effluent. So, some of the nitrate was immediately reduced by gentrification.

The result from the activity measurement in ZIN wetlands revealed that the potential for nitrification and denitrification in the wetland was very high. Even though the wetlands have high potential for denitrification, the TN removal from the wetlands was very low. This is because the carbon source for denitrification in the wetland was very low.

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