Dow's Sustainable Water Use Strategy

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Abstract

Dow has set ambitious goals to reduce its dependency on fresh water supply by enhancing water reclamation and reuse. For its six water stressed sites globally, Dow aims to reduce its fresh water intensity by 20% in 2025 (compared to 2015). At its second largest production site in Terneuzen (the Netherlands) Dow and Evides Industriewater rolled out a plan to eliminate the structural intake from remote fresh water sources. Intensive research is ongoing to establish the use of a constructed wetland in combination with a mild desalination process.

Keywords: water stress, water reuse, constructed wetland, mild desalination

Introduction

Access to and availability of fresh water is a prime requisite for operating chemical plants. Dow has large scale industry parks in many countries, some of these located in water stressed areas. Global challenges will increase the pressure on fresh water provision. Among these are climate change (causing sea level rise, increasing salinization of coastal areas and weather extremes), but also demographic developments (more people demanding more food and energy) and the transition to fossil-free sources for raw materials and energy, while striving for a CO_2 neutral society by 2050.

Dow has set ambitious goals to reduce its dependency on fresh water supply by enhancing water reclamation and reuse. For its major six water stressed sites globally, Dow aims to reduce its fresh water intensity by 20% in 2025 (compared to 2015). At its second largest production site in Terneuzen (the Netherlands), Dow and Evides Industriewater rolled out a plan to eliminate the structural intake from remote fresh water sources. With a total fresh water demand to run its processes of 22 million m³/yr Dow Terneuzen claims 70% of the total water use in the local watershed. Therefore in the past decades, Dow and its partners have already implemented various measures to reduce Dow's water footprint. As a result (Fig 1) most of Dow's water supply (75%) currently originates from sustainable sources. However, 4-5 million m³/yr of water is supplied from the 120 km remote Biesbosch area – being the major source for potable water supply in the southwest region of the Netherlands. Dow strives to eliminate that water source for industrial applications. In the EU funded FP7 E4Water project intensive studies were carried out to investigate treatment of a variety of regional raw water streams, providing significant knowledge on raw water characteristics and treatment opportunities (Ref 1, 2).



Figure 1. Dow Terneuzen – raw water sources (2020)

In 2019 Dow and Evides Industriewater have agreed upon a new contract for water supply to the Terneuzen site, meeting Dow's targets for reliable water supply and sustainability. As a part of the agreement Dow Benelux BV and Evides Industriewater will by 2024 implement a facility that allows the reuse of almost 8 million m³ annually of a mix of waters from various sources. Water will be supplied from the Terneuzen municipal treatment plant, Dow's wastewater treatment facility, and rainwater collected from the Dow premises and its periphery. The technical concept for this new water production unit (Fig 2) was developed in close collaboration between water experts from Dow Water Solutions (since 2019 DuPont Water Solutions), Dow Environmental Tech Centre and Evides (ref 3), and comprises the use of a constructed wetland in combination with a mild desalination process to produce a high quality industrial water. To validate the concept and to determine key design parameters for a full scale facility, an intensive two year research program is being conducted. This abstract is predominantly focusing on the constructed wetland as a pre-treatment step for the consecutive mild desalination step. In this research project also the regional Water Board Scheldestromen participates, being particularly interested in the wetland functionality to reduce micro pollutants from pharmaceutical and agriculture run-off, which are typically poorly degraded in conventional treatment plants.



Figure 2. Scheme of the water treatment concept.

Concept and Research Plan

During the pilot research the entire concept of the foreseen treatment will be tested. The set-up can be divided into two major steps, being a constructed wetland as a pre-treatment for the two treated wastewater streams from both municipal and industrial origin, and next a desalination train. The mild desalination comprises three separate unit operations:

- Ultrafiltration (UF) for the removal of suspended solids, using RO concentrate for backwash;
- Ion Exchange Resins (IER) for softening (hardness removal) and scavenging nutrients and TOC;
- Reverse Osmosis (RO) for removal of residual ions (Na⁺, Cl⁻, etc.), providing concentrate reuse in IER and UF.

The preceding **constructed wetland** is primarily designed to provide a biologically stable effluent making the mild desalination train significantly less susceptible to biofouling, thereby saving on use of chemicals for cleaning, enhancing water recovery, and resulting in a lower energy demand. Moreover, the wetland will help reducing nutrients (ammonia, phosphorus, nitrate, and organics), suspended solids and poorly degradable components (pharmaceuticals, pesticides, etc.).

The constructed wetland of the type Horizontal Sub-Surface Flow (HSSF) consists of two separate wetland cells (350 m² each), which can be fed with municipal or industrial treated wastewater, in parallel or in series. Hydraulic residence time can vary between 12 and 24 h, with flowrates up to 10 m³/h. In a

full scale HSSF design the wetland has a vertical inlet section to capture incoming suspended solids. In the pilot the water flows directly in horizontal direction below surface through a bed filled with Argex clay grains, and planted with *Phragmites australis* (common reed). Both units have three zones with facultative aeration supplied by an air distribution grid (Forced Bed Aeration; FBA®), a concept invented and patented by Naturally Wallace Consulting (USA) and licensed in the Benelux by Rietland bvba. In the middle section of each wetland cell, specific functionalities can be tested: the so-called "North wetland" has a zone where a carbon source can be dosed for biological nitrate removal, whereas the "South wetland" has a zone where biochar was mixed in between the Argex clay grains – in the biochar zone adsorption phenomena can be studied with a specific interest for micro pollutants.



Figure 3. Wetland pilot aerial view, configuration.

Typically, full scale wetlands have little instrumentation and control as it is believed that when well designed the natural processes occurring in the system proceed without human interaction. Depending on the design and wetland type, seasonal variability may impact the overall performance. As industrial processes have a consistent demand throughout the year, each treatment system needs to be robust and little impacted by seasonal variations. Therefore Rietland designed a high-rate wetland system with biological processes mostly running subsurface (ref 4). To collect sufficient data from the pilot, both wetland units are well instrumented, as shown in figure 4. Flowrates can be varied and level of aeration (with dissolved oxygen (DO) sensors) can be controlled automatically – furthermore on-line instruments are installed to monitor nitrogen and organics removal. An intensive grab sample and analysis program is backing up automatic monitoring and providing detailed information on organics and trace constituents.

Specific mention should be made of biofilm monitoring tests. Biofilm growth is supposed to be enhanced by the presence of nutrients, especially phosphorus, degradable COD, and nitrogen. Biofilm monitoring tests are therefore critical to assess the biofouling reduction potential of the wetland system prior to downstream process steps and can be directly used for a comparison with alternative technologies like a BODAC (Biological Oxygen Dosed Activated Carbon). This particular measurement device, developed by WLN (ref 5), consists of a stack of 20-30 glass rings, blinded against direct sunlight, and receives a constant flow of water. During a period of 10 weeks two of the rings are removed each week and analysed on ATP (Adenosine Tri Phosphate), indicating the presence of biological growth.



Figure 4. Wetland instrumented design

Results and discussion

In the first year of pilot operation basic design parameters were investigated. Wetland North was receiving treated effluent from municipal origin, while wetland South received industrial effluent. Typical influent parameters of each are given in Table 1 and removal rates of some pollutants during an HRT (hydraulic retention time) of 12 hours and double retention time (HRT 24 hours) are shown in Table 2. During the 12h HRT experiments the ratio of C (carbon) to N (total nitrogen) was kept at 4.0.

	Conductivity (µS/cm)	Turbidity (NTU)	P-PO₄ (mg/l)	NH₄ (mg/l)	pН	Temperature (°C)	Nitrate (mg/l)	TOC (mg/l)
Effluent Terneuzen	1500-2750	6-10	2-4	3.4-9	8-9	12-20	27-33	12-15
Effluent Biox	890-1500	0-3	0.4-2	0.4-1.6	7-7.5	20-35	8-20	10-15

Table 1. Characteristics of municipal (Terneuzen) and industrial (BIOX) treated wastewater

Table 2. Pollutants removal with HRT 12h (COD:N=4.0) and both wetlands in series (HRT 24h)

COD		NH4-N		NO3-N		TN		O-PO 4	
%		%		%		%		%	
HRT 12h	HRT	HRT 12h	HRT						
(COD/N=4)	24h	(COD/N=4)	24h	(COD/N=4)	24h	(COD/N=4)	24h	(COD/N=4)	24h
0-11	25-	95-100	95-	40-50	45-	50-60	55-	65-75	80-
	35		100		55		65		90

Through PLC and DO sensors, the dissolved oxygen level in each zone of both wetlands can be controlled through time-based aeration and/or DO concentration in the water (Figure 4). Using various aeration settings (100%on, 50%on-/50%off,1-2, 2-3, 3-4 and 2-3 mg/L in zone 1 and 0 mg/l in zone 2&3), the optimum setting was found with respect to removal performance and energy use. For most purposes, controlling DO levels at 2-3 mg/L appeared to be optimal. However, ammonium-nitrogen was

completely nitrified at all aeration settings, while organics had a partial removal only. Phosphorus removal, which mostly occurs via adsorption, is almost complete after 24h HRT.

Furthermore, different dosages of C-source (COD/N = 0, 2.0, 3.5 & 4.0) were applied in wetland North and consistent removal up to 50-60% in total nitrogen appeared possible with moderate carbon dosing (COD/N =4.0, Figure 5). During C-dosing, the aeration was switched off in the middle section of the wetland to create anaerobic circumstances for denitrifying bacteria.

Later, both wetlands were connected in series (North \rightarrow South) to check double retention time; HRT 24 hours. Figures 6a, b and c show the concentration of nitrogen (NH₄-N, NO₃-N and TN (sum of NH₄-N and NO₃-N while ignoring organic N)) when wetlands are in series using mixed feed i.e. 50% municipal of Terneuzen feed and 50% BIOX feed. During this, no C-source was applied to any wetland. Ammonium nitrogen (NH₄-N) was completely nitrified in this case too and the removal of NO₃-N and TN from North to South was also significant.



Figure 5. Total nitrogen removal in wetland North versus different carbon dosing



Figure 6. (a, upper left) the concentration of NO₃-N, (b, upper right) NH₄-N and (c, lower) TN in HRT 24 hours (wetlands in series)

Figure 7 shows the COD concentrations for similar settings (wetlands in series). COD was removed in both wetlands - however, the average removal in wetland North was higher than in South. In general, decay is first order, so it could be possible that most of the COD is removed in North (biodegradable part) and what is left for South is mostly non-biodegradable.



Figure 7. COD concentration in wetland North and South in HRT 24 hours

Figure 8 shows the visual results of 10 weeks of biomonitoring, operating both wetlands in series (influent at wetland North, effluent from wetland South). Already after one week the wetland influent shows major fouling, while the effluents still are clear. Then after ten weeks some fouling is visible at the effluent of the North wetland, while the final effluent is still clear. Cumulative data of ATP measurements are presented in Figure 9, showing a steady increase after the first bed and limited growth after the second bed. The longer residence time and absorption capabilities of the beds in series clearly have an enhancing effect on reducing the biofouling potential.



Influent North

Effluent North

Effluent South

Effluent North

Effluent South





Figure 9. Biofilm monitor with wetland North and South in series - ATP measurements

While in the first year of the pilot research the wetland and mild desalination trains were operated in parallel – during the second year of the trial both trains will be connected to show the impact of a preceding constructed wetland on the performance of membrane and ion exchange resin units. Biofilm monitoring experiments will be extended to include seasonal variations and downstream impact.

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References

- Groot, C.K., Van den Broek, W.B.P., Loewenberg, J., Koeman-Stein, N., Heidekamp, M., and De Schepper, W. (2015). Mild desalination of various raw water streams. Water Science and Technology Vol 72 No 3 pp 371–376. DOI: 10.2166/wst.2015.228.
- Löwenberg, Jonas ; Baum, Jörn Ansgar ; Zimmermann, Yannick-Serge, Groot, Cornelis; van den Broek, Wilbert; Wintgens, Thomas, 2015. Comparison of pre-treatment technologies towards improving reverse osmosis desalination of Cooling Tower Blow Down. Desalination 357, pp. 140-149. DOI information: 10.1016/j.desal.2014.11.018
- 3. https://onlinelibrary.wiley.com/doi/full/10.1002/cite.201900042
- 4. D. Van Oirschot & S. Wallace & R. Van Deun Environ Sci Pollut Res (2015) 22:12870–12878
- 5. Van der Maas, P., Majoor, E, Schippers, J.C., (2009) Biofouling control by Biological Activated Carbon Filtration: a Promising Method for WWTP Effluent Reuse. IWA Membrane Technology Conference and Exhibition. ID 95, session: domestic wastewater reuse.