



Safer water for future generations

Feasibility Trial Report

PWNT

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1 Introduction

This report is a summary of treatability trials carried out by Arvia Technology Ltd on site at PWNT in the Netherlands, and then subsequently at Arvia Technology's laboratory in the UK. The purpose of the trials was to investigate the suitability of the Nyex™ treatment system to remove DOC, colour and micropollutants initially from two different water sources: surface water- IJssel Meer (IMW) and ion-exchange (IX) brine. Whilst on site another waste stream was identified for treatment-brine from an Electrodialysis unit (ED brine).

1.1 PWNT

PWNT is owned by the Dutch water utility PWN. This technology division aims to share the utility's experience gained over 90 years and realise the innovations in water treatment worldwide. The R&D programmes carried out by PWNT have led to the development of sustainable and efficient solutions in various technologies such as advanced oxidation, ceramic membrane applications, ion-exchange (IX) and others.

1.2 Arvia Technology

Arvia's Nyex™ treatment system is a water and wastewater treatment system designed to reduce recalcitrant organics and remove problem pollutants as well as colour from contaminated water.

Arvia's patented advanced oxidation technology combines adsorption and in-situ electrochemical regeneration within a single continuous treatment solution. The influent flows downward through a packed bed of proprietary adsorbent, Nyex™, during which organic contaminants are adsorbed onto the surface and a low voltage electric current, proportional to the organic concentration is passed through it. This causes the adsorbed organics to be oxidised and the surface of the Nyex™ to be regenerated in-situ for further adsorption without interruption or replacement.

The treated water flows from the bottom of the cell where it can either be re-used in-process or the treated water can better meet current and future water quality standards. A schematic of the modular design of the Nyex™ treatment cell is shown below.



Figure 1. Modular design of Arvia's Nyex™ treatment system which treats water by adsorbing organic contaminants from the influent as it percolates the packed bed of Nyex™ particles, and the simultaneous passing of current ensures in situ oxidation of the adsorbed organic.

1.3 Introduction to the application

The PWN Andijk III site in the Netherlands produces 120 million litres of drinking water. The treatment chain currently is illustrated in Figure 2.

The aim of the trial was to demonstrate and evaluate the effectiveness of the Arvia process on surface water IMW and the brine from IX and ED. The KPI's to be evaluated and used as a means of suitability for treatment are DOC, micropollutants and colour.

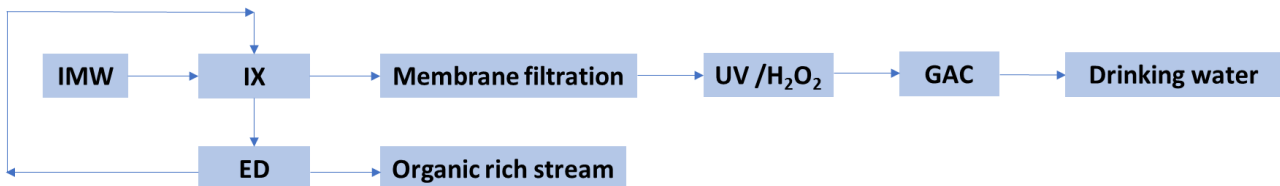


Figure 2. Andijk III site treatment chain feeding from surface water IMW

Table 1 below displays key process water characteristics of the three waste streams to be treated and obtained from PWNT.

Table 1. Process water characteristics

Parameter	IJssel Meer Water (IMW)	Ion-Exchange Brine (IX)	Electrodialysis Brine (ED)
TOC (mg/L)	2-6	200-500	550
Conductivity (mS/cm)	-	17-49	15.03
pH	7.5	9	9
Cl ⁻ (g/L)	0.095-0.135	Up to 17	1.2
HCO ³⁻ (g/L)	0.13-0.16	2-7.3	2-3
SO ₄ ²⁻ (g/L)	0.047	3-8	7.9
Various micropollutants (µg/L)	0.5-1.1	0.5-1.1	0.5-1.1

2 Treatability Study

2.1 Trials set-up

Two types of test unit configuration have been used as illustrated hereafter.

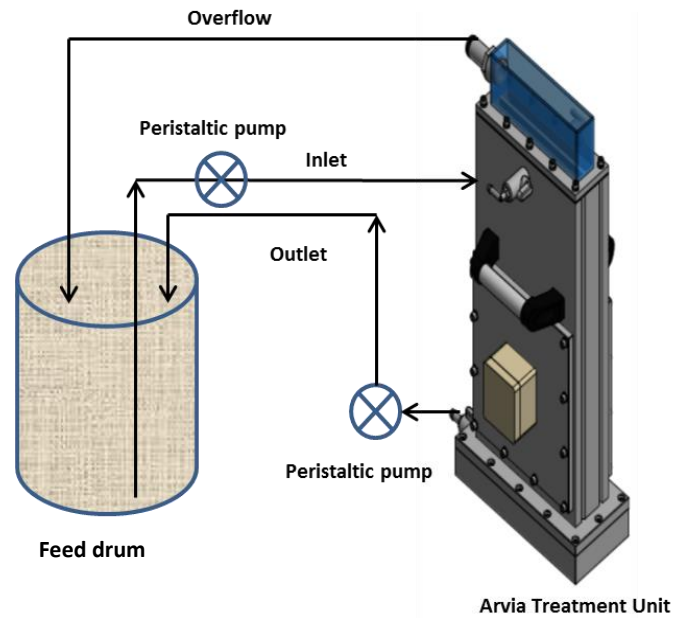


Figure 3. Schematic of the recirculation setup used for some of the treatability trials.

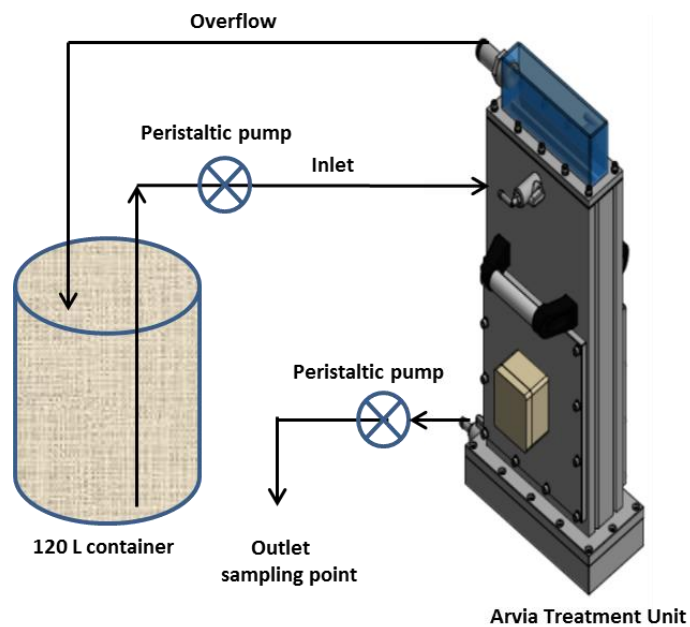


Figure 4. Single-pass set up used for some of the trials.

2.2 Trial specifics

A series of trials were carried out to offer a viable treatment solution for the IJssel Meer surface water, IX brine and ED brine. A summary of the trials conducted on-site is detailed in Table 2 below.

Table 2. Summary of the trials carried out

Trial no.	Wastewater	Flow rate (L/h)	Current density (mA/cm ²)	Flow configuration	Trial duration(h)
A1	IMW	2	1.25	Re-circulation	25
A2	IMW	2	1.25	Single-pass	68
A8	IMW	2	0.313	Single-pass	4
A9	IMW	2	0.625	Single-pass	4
A10	IMW	2	Pulsing -0.625	Single-pass	8
E5	ED-pH 1	2	25	Re-circulation	4
E6	ED-pH 1	20	25	Re-circulation	4
E8	ED-pH 0.5	2	25	Re-circulation	4
A5	ED	2	2.5	Re-circulation	17
E1	IX-pH2	2	25	Re-circulation	2
E2	IX-pH2	20	25	Re-circulation	2
E3	IX-pH2	20	25	Re-circulation	4
E4	IX-pH2	2	25	Re-circulation	4
E7	IX-pH 0.5	2	25	Re-circulation	4
A3	IX	2	2.5	Re-circulation	17
EA1	IX-pH 1	2	25,2.5	Re-circulation	28

2.2.1 Comments to Table 2

2.2.1.1 Trials with E indicate use of a Nyex™ 1-20e system and trials with an A indicate a Nyex™ 1-20a system.

2.2.1.2 Details of the trials

- pH adjustment of the brine was carried out for the trials with the Nyex™ e system. This was due to the high concentration of carbonates in the wastewater sample which reduces the efficiency of the Nyex™ e system.
- Analysis of the samples that were carried out include:
 - a. DOC: UVT₂₅₄ was measured and an existing correlation provided by PWNT was used to allow UVT₂₅₄ to act as a surrogate parameter for DOC on the IMW whilst on site at PWNT
 - b. Micropollutants: external laboratory analysis for micropollutants have been used. In addition, some DOC samples were taken for external laboratory analysis to validate the inhouse data.

2.3 Trial results

2.3.1 Ijssel Meer Water (IMW)

The main performance indicator for the IMW was micropollutant removal. However as onsite micropollutant analysis was not available DOC was used as a performance indicator for trials A1 and A2.

Table 3. Summary of results

Trial no.	Wastewater	Flow rate (L/h)	Current density (mA/cm ²)	Flow configuration	Treatment result
A1	IMW	2	1.25	Re-circulation	65% DOC removed
A2	IMW	2	1.25	Single-pass	See section 2.3.1.1
A8	IMW	2	0.313	Single-pass	*
A9	IMW	2	0.625	Single-pass	See table 4 below
A10	IMW	2	Pulsing -0.625	Single-pass	See table 4 below

*Insufficient volume generated for sample.

2.3.1.1 Trials A1 and A2

Both trials A1 and A2 were run on a NyexTM-a system with the IMW surface water. The current was applied for the full duration of trial A1.

As can be seen on figure 5, the DOC dropped immediately from 5.2 to 1.8 mg/L. This represents a 65% removal of the DOC though this most likely represents predominantly adsorption. It can be then seen that the DOC increases over time. It was then decided to investigate the adsorption capability of the Nyex for the low concentration IMW surface water to determine the impact of adsorption relative to oxidation.

Subsequently, a single-pass trial with no current was carried out in A2 to allow the Nyex to be fully saturated. Once breakthrough was achieved (at 59 hours), the current was applied. It is observed on figure 6 that the DOC increased after the current was applied. The increase in DOC may be attributed to Nyex attrition due to the amount of current that is being applied.

With the focus on this waste being a low-concentration micropollutant removal not only is the amount of current applied key but also the frequency of current application (pulsing). These two factors were further investigated in trials A8, A9 and A10. It is also important to note that even if the DOC has increased, the micropollutant may be fully mineralised as has been in the case in previous applications. As on-site analysis of micropollutants was not available, it was difficult to ascertain the micropollutant removal performance and as such the DOC correlation was used as a performance parameter.

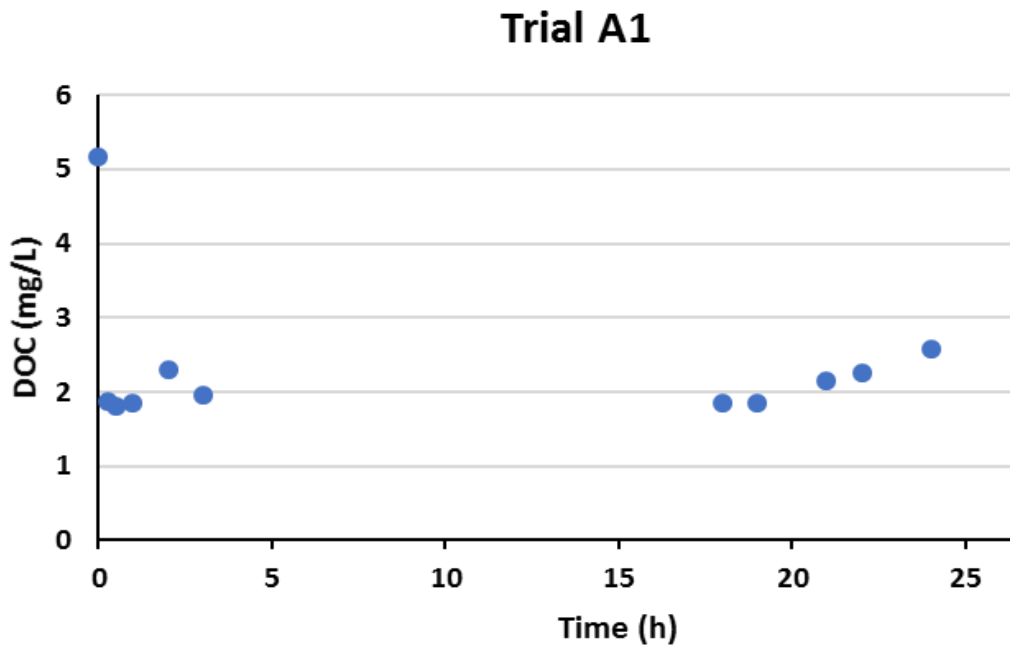


Figure 5. Trial A1 DOC profile against time

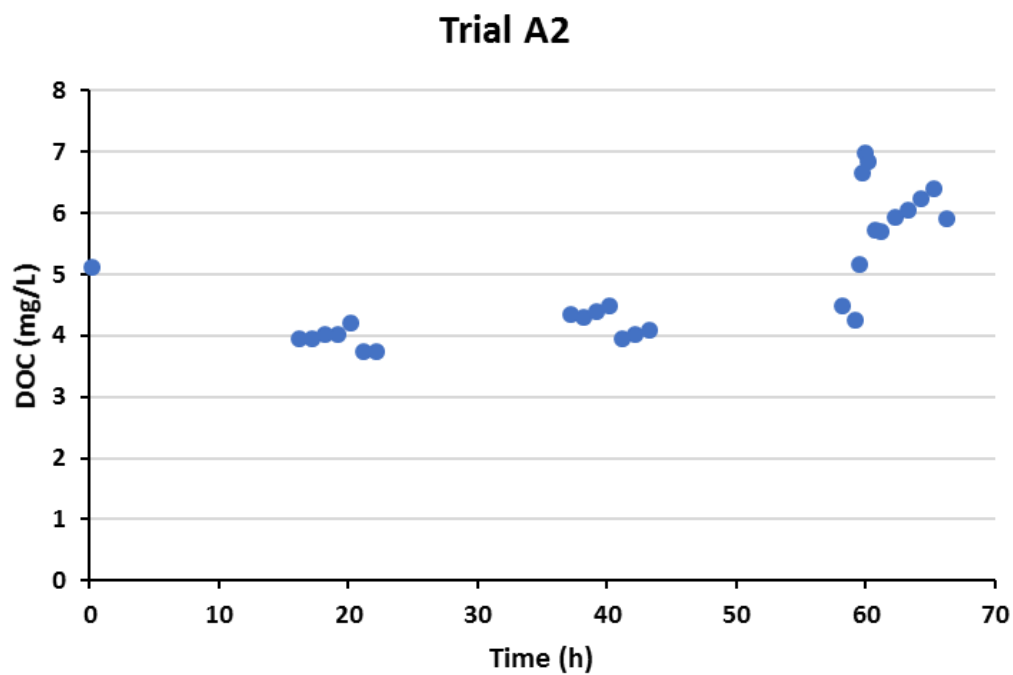


Figure 6. Trial A2 DOC profile against time

2.3.1.2 Trials A9 and A10

Table 4. Micropollutant analysis results

Compound	Removal		
	Saturation	A9	A10
10,11-trans diolcarbamazepine	57.8%	63.0%	60.1%
acetylsulfamethoxazole	100.0%	100.0%	100.0%
atenolol	100.0%	100.0%	100.0%
bisoprolol	100.0%	100.0%	100.0%
carbamazepine	91.1%	97.8%	97.0%
coffeïne	86.8%	1.1%	35.6%
fenazon	-40.1%	81.6%	88.7%
ifosfamide	0.0%	0.0%	0.0%
iopromide	75.3%	100.0%	47.0%
lidocaïne	100.0%	100.0%	100.0%
lincomycine	100.0%	100.0%	100.0%
losartan	100.0%	100.0%	100.0%
metformin	38.0%	76.4%	57.9%
metoprolol	100.0%	100.0%	100.0%
oxazepam	91.3%	100.0%	100.0%
primidon	-5.0%	20.0%	15.0%
propranolol	100.0%	100.0%	100.0%
sotalol	100.0%	100.0%	100.0%
sulfamethoxasol	48.2%	88.5%	86.0%
temazepam	85.7%	76.2%	38.1%
theophylline	96.6%	100.0%	100.0%
trimethoprim	100.0%	100.0%	100.0%
acesulfaam	1.5%	21.9%	20.6%
cyclamaat	7.8%	18.8%	14.1%
saccharine	14.1%	25.0%	29.7%
sucralose	100.0%	19.0%	-51.8%

2.3.1.3 Comments to Table 4

For trials A9 and A10 a series of micropollutants, both pharmaceutical and sweeteners were analysed.

From this selection, there were some that were not detected in the start sample or there was no quantification possible by the lab-these have been omitted.

Initially, a saturation test was carried out where the no current was applied to the system. Current was then applied in trial A9 and then the same trial was carried out but with the current pulsed into the system in A10. The benefit of investigating the use of pulsing is that the operational costs would be reduced.

As can be seen in table 4 above the removal rates are high for the pharmaceuticals with most compounds achieving over 90% removal. The final four sweeteners have also shown removal, further work would need to be conducted to improve the efficiency of the Arvia process in removing the sweeteners, historically we have carried out work on sweeteners and have achieved much higher removal rates. In addition, the amount of current that was applied to the system was minimal therefore this could be a contributing factor to the limitation in treatment of the sweeteners. The concentration of the sweeteners was in the region of micrograms whereas the pharmaceuticals were in the range of nanograms, this further supports the above-mentioned point.

In the case of the fenazon and primidone, we can see for the saturation that there is an increase in concentration. A possible explanation could be the desorption of previously adsorbed concentrations of these compounds from previous trials that were run on the same Nyex, however on application of current we can see that removal occurs.

In the case of sucralose, we can also attribute the increase in concentration to desorption of previously adsorbed organics from previous trials conducted on the same Nyex, however it may be the case that destruction of the sucralose compound requires more current density. It is also worth noting that trials on the IMW surface water for micropollutant removal that were carried out were unoptimized, please see section 3 for recommendations.

2.3.2 Electrodialysis Brine (ED)

The main performance parameters for the ED brine were DOC and colour.

Table 5. Summary of results

Trial no.	Wastewater	Flow rate (L/h)	Current density (mA/cm ²)	Flow configuration	Treatment result
E5	ED-pH 1	2	25	Re-circulation	24% DOC removed, Colour removed
E6	ED-pH 1	20	25	Re-circulation	22% DOC removed, Colour removed
E8	ED-pH 0.5	2	25	Re-circulation	*
A5	ED	2	2.5	Re-circulation	42% DOC removed, Colour partially removed

*Data points erroneous

2.3.2.1 Trials E5 and E6

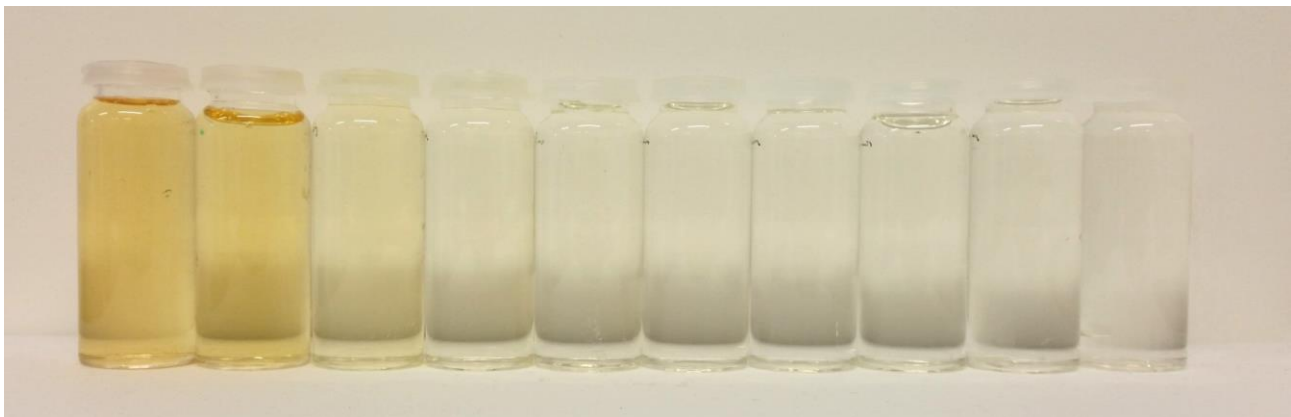


Figure 7. Trial E5 treatment profile

Both trials E5 and E6 were run in recirculation mode and show a 22-24% reduction in DOC with complete colour removal.

The purpose of these two trials was to see if the ED brine could be treated via the Nyex™ 1-20e system, by pH adjusting to 1, the aim was to drive off the carbonate present in the sample. Carbonates are notorious for reacting with the OH radicals generated in the process instead of carrying out oxidation of the organics.

Despite acidifying the sample, it appears that the residual concentration of carbonates in the sample are still inhibiting the efficiency of the Nyex™ 1-20e system.

2.3.2.2 Trial A5



Figure 8. Trial A5 before(left) and after(right).

Trial A5 was a trial that was conducted on the ED brine to investigate the treatment using the Nyex™ 1-20a system.

In single-pass mode operation little DOC was removed from the sample due to the concentration of DOC in the sample.

However, for the recirculation mode operation a 42% DOC removal was achieved, and the colour was also partially removed as can be seen in figure 8 above.

2.3.3 Ion-Exchange Brine (IX)

2.3.3.1 Trials E1 and E2

Both trials E1 and E2 were run in recirculation mode and show ca. 25-26% reduction in DOC. The Nyex™-e system was utilised, and the system relies more on oxidation rather than adsorption for DOC removal. The two trials were run at different flowrates to understand how the organic content in the brine wastewater behaves. For both trials the colour of the waste was completely removed as can be seen in figures 9 and 10. In terms of the DOC removal, although the IX brine was pH adjusted to 2, there may still be enough carbonate present which prevents the system from oxidising the remaining fraction of organics. It was then suggested to run the trials for a longer period.



Figure 9. Before(left) and after treatment(right) for E1



Figure 10. Before(left) and after treatment(right) for E2

2.3.3.2 Trials E3 and E4

Trials E3 and E4 were essentially the equivalent trials carried out of E1 and E2 but for a longer period. The trend in DOC removed is similar. However, it appears that there is no improvement in DOC treatment running for longer periods despite once again the colour of the sample disappearing as was the case in previous trials.

2.3.3.3 Trial A3

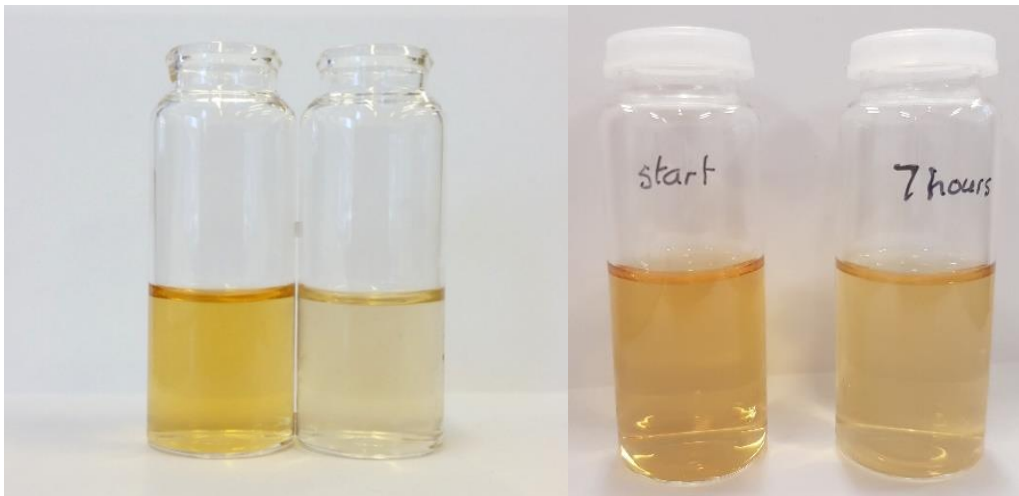


Figure 11. Left(recirculation) and Right(single-pass).

Trials A3 a was run with the IX brine using the Nyex™ 1-20a system. A3 was initially run in single pass mode but as expected for this concentration of DOC the removal was quite low. Subsequently a recirculation trial was run and achieved a 34% reduction in DOC, the colour was also partially removed. This means that a longer residence time is needed in the system to treat the organic contaminants and further indicate that the nature of the organic is more hydrophilic than hydrophobic. The samples for trial A3 can be seen above in figure 11.

2.3.3.4 Trial EA1

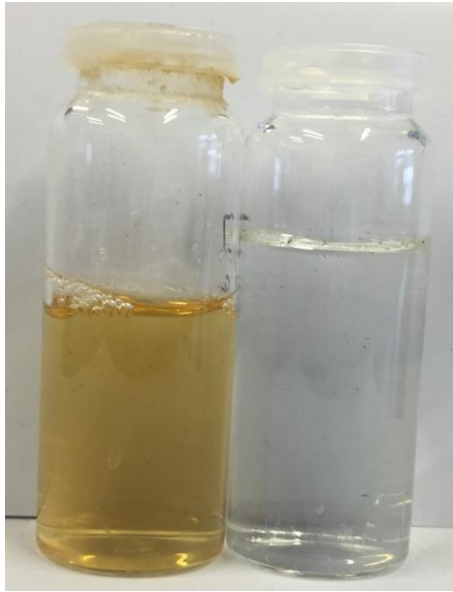


Figure 12. Trial EA1 before(left) and after(right).

Trial EA1 was conducted to see if more DOC could be removed with a combination of the Nyex™ e system and Nyex™ a system in series. The idea being that the E-system takes out the first portion of the DOC and colour and the A-system takes out the remaining fraction. Initial results have shown an increase treatment with 52% DOC removed and complete colour removal.

3 Conclusions

3.1 IMW water

For the trials conducted on the IMW surface water the Nyex treatment system has proved to be successful in removing micropollutant concentrations of most of the compounds tested, further optimisation on a larger unit would allow us to improve the treatment. The further optimisation and investigation into pulsing for the IMW on a large-scale unit would also be useful in determining the OPEX savings achieved via pulsing.

3.2 IX and ED water

In conclusion, for both the IX and ED brine the Nyex treatment systems can remove a fraction of the DOC and achieve complete colour removal, either by one or both treatment systems in conjunction, the maximum DOC removal achieved was 52% with complete colour removal on a lab-scale trial.

The nature of the brine wastewater matrix is critical, the Arvia treatment system can remove a fraction of DOC which is hydrophobic in nature. However there also seems to be a recalcitrant fraction of the DOC that is strongly hydrophilic, this means that it is difficult to adsorb onto the Nyex and hence the removal rate was low. There is also a possibility that a fraction of the DOC is recalcitrant and resistant to oxidation. This coupled with the fact that the neat sample contains a large concentration of carbonates could be the reason for the limitation in treatment.

3.3 Way Forward

To optimise treatment in all wastewater streams, it is proposed to carry out a long-term pilot study on-site at PWNT. We know that the system benefits from scale-up and have seen in previous trials the enhancement of treatment at pilot and subsequent full scale.

3.4 Dates of trials

PWNT in Andijk (The Netherlands): 16/04/18-20/04/18

Arvia Technology in Runcorn (UK): 01/05/18-29/06/18

3.5 Acknowledgements

This research has been carried out within the Interreg 2 Seas project DOC2C's. The DOC2C's project is a joint European collaboration with project partners from the water industry and universities in the 2 Seas Area to research and to exchange the results on Dissolved Organic Carbon (DOC) removal. The DOC2C's consortium consists of PWN Technologies R&D (NL), South West Water (UK), De Watergroep (BE), Lille University (FR) and Delft University of Technology (NL). As DOC is a growing problem in surface water treatment, Interreg, the European Regional Development Fund, the Dutch Government and the Province of North Holland acknowledge the importance and necessity of the DOC removal in the 2 Seas area by co-financing this project.