

NOM-removal at SWTP Andijk (Netherlands) with a New Anion Exchange Process, called SIX[®]

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Abstract: The new developed ion exchange process SIX presents an advanced solution for a world-wide challenge: How to remove NOM/DOC as a first step in surface water treatment to improve efficiency of downstream processes and to improve water quality. Besides the possibility to treat water containing suspended matter another advantage is the fact that the process has advanced to an economical and technical feasible process, guaranteeing a stable water quality, resulting in a large tolerance for flow fluctuations and relatively low contact times and small resin inventory. Most important advancement however is that almost every commercially available resin can be used creating the desired flexibility in suppliers for water supply companies. This paper describes the process and generates advantages and disadvantages compared to conventional technologies leading to the world first full-scale application with a capacity of 5500 m³/h.

Keywords: NOM-removal, DOC-removal, ion exchange, regeneration

Introduction

Ion exchange (IX) is considered to be both an adsorption process and a sorption process (Wachinski, 2006). The term ion exchange describes the unit process of IX, which is widely used in water treatment to remove unwanted contaminants. The most common application of IX is softening, but there are many kinds of resin, and anion IX resins can be used for the removal of anions like nitrate, DOC, and arsenate. IX has been introduced by the WHO as a nitrate removal technology and approved as the Best Available Technology (BAT) for nitrate removal by US EPA. Cation ion-exchange refers to the removal of cations, such as calcium and magnesium.

Wachinski and others argue that the role of IX in water treatment is changing. This is because of the proposed brine discharge legislation in California, Montana, and Texas and also because of advanced membrane technologies, AOP and the need for many utilities to lower DBP formation potential. Ion exchange processes generate a waste stream which is usually referred to as a brine, because salt is most commonly used to regenerate the IX resin. This waste water contains high concentrations of the contaminant ions and high concentrations of regenerant solution, usually sodium chloride. Management and disposal of these brines present a formidable challenge to engineers, just as is the case for NF/RO membrane concentrates. Engineers must not only select the proper pre-treatment and IX process but also the proper brine recovery or brine disposal option. Conventional alternatives like coagulation or nanofiltration, which are alternatives for DOC removal, also generate waste. In some situations, these waste streams are more difficult to discharge or dispose of than the brine of an anion IX process. This problem is very site specific and depends on local legislation and the water characteristics.

Anion IX however offers a very good opportunity for enhanced removal of organic matter for source waters that contain medium to high concentrations of NOM because the majority of compounds which make up NOM are negatively charged.

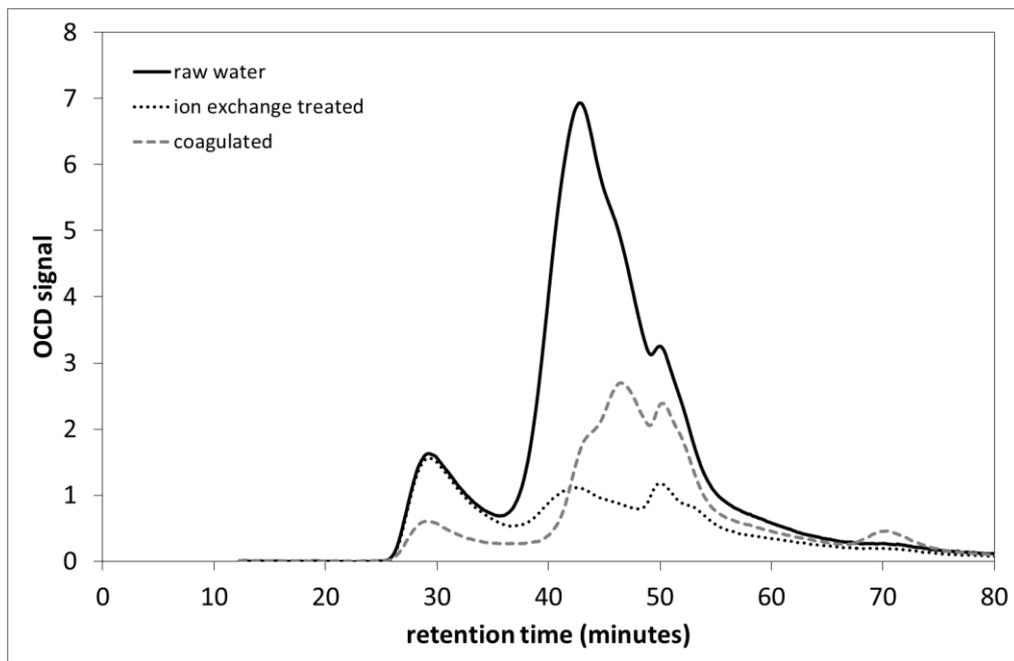


Figure 1, SEC-OCD chromatogram of ion exchanged and in-line coagulated IJssel Lake water

The size exclusion chromatography-liquid chromatography-organic carbon detection (SEC-LC-OCD) method is a powerful analytical tool to characterize organic matter and to observe relative differences in DOC. The SEC broadly groups the organics into five fractions: biopolymers (MW \gg 20,000 g/mol), humics (MW \sim 1,000 g/mol), building blocks (MW 300-500 g/mol), LMW acids and LMW neutrals (MW < 350 g/mol) (in the order of retention time). Two detectors, organic carbon detector (OCD) and ultraviolet detector (UVD) detect the organics. The OCD spectrum is used to determine the total mass of organic carbon, whereas the UVD spectrum detects only the UV adsorbing species (i.e., double bond carbon), the so-called chromophoric DOM. Figure 1 shows an example of an OCD signal where the same surface water is treated with enhanced coagulation and anion IX. It is clear that enhanced coagulation removes a part of the biopolymer fraction (around 30 minutes retention time) and a small portion of humics (around 40 minutes retention time). The IX removed most of the humics with the highest UVT_{254nm} molar absorption coefficients and LMW fractions (around 40 and 50 minutes retention time) but it has almost no impact on biopolymer removal. As a result, the UVT 254nm for enhanced coagulation was 82 percent while anion IX achieved a treated water UVT of 94 percent.

Problem description

Some waters can have elevated concentrations of DOC, especially sources like surface waters that are under the influence of secondary effluent, recreation, heavy population, farming and industry. In places like in the United Kingdom and Scandinavia DOC levels are inclining due to climate change. For these types of water, IX as a pre-treatment is of interest because the removal of colour and DOC by IX will increase the efficiency of all downstream processes, including coagulation, membrane filtration, AOP and GAC. With these waters, there is also

suspended and colloidal matter and this makes it nearly impossible to use standard state-of-the-art, fixed bed IX columns. This is because these beds will foul quickly (i.e., head loss build-up) with the suspended matter. When this happens, the ion exchange bed starts to function as a filtration bed rather than as an adsorption media.

Available technologies to treat such heavy polluted waters are based on fluidized bed reactors or on totally-mixed reactors with very high concentrations of resin (>400 mL/L), like in the MIEX® process, (an acronym for Magnetic Ion Exchange, manufactured and commercialized by Orica) or in fluidised bed reactors to prevent entrapment of suspended matter. In the fluidised bed and the MIEX®-process the bed volumes treated until regeneration are designed to be as high as possible with the goal to remove as much of the pollutants as possible before regeneration, thus lowering the salt consumption needed for regeneration [Slunski, 1999]. This approach can have a few disadvantages depending on the treated water that makes it less attractive to use (i.e., more expensive), but more importantly, for some waters, the anion ion exchange resin of the MIEX® process which is used to remove dissolved organic carbon (DOC) from raw surface waters is sometimes not feasible. This is because these waters often contain phosphates, which will be adsorbed, and with the large detention times (used to minimize the number of regenerations) and porous resin beads, the perfect environment for bacteria to grow in is created because the resin is now a source of carbon and phosphorous. The biofilm that forms on the resin, blinds the active groups of the resin, and this is referred to as “resin blinding”. Resin blinding occurs slowly but can lead to serious problems. Besides losing adsorption capacity [Wachinski, 2006], this leads to the need to operate with a higher resin concentration or longer contact time [Verdickt, 2011; Cornelissen 2009], thus increasing operational costs and/or lowering plant capacity, and after time, the biofilm itself starts to release organic matter or adenosine triphosphate (ATP) that can be detrimental to downstream processes [Cornelissen, 2010], especially membranes.

To overcome resin blinding, fixed bed or fluidised reactor systems are flushed with a high pH solution on a periodic basis to kill and dissolve the biofilm as much as possible. These fixed beds, however, like mentioned before, cannot treat waters with suspended matter. For the MIEX® processes, which use a hydrophobic resin, it is not possible to use high pH (hydroxide ions) to control biofilm development because the resin is not resistant to hydroxide, and with exposure would begin to fall apart over time, thus shortening the lifetime of this relatively expensive resin.

These issues have led to the development of a new ion exchange process [Galjaard, 2009] by PWNT. Compared to the other described ion exchange processes treating waters containing suspended matter, the ‘single pass’ or ‘suspended’ ion exchange process (SIX®) achieves full control of the adsorption process without (serious) ‘blinding’ the resin or producing biomass (www.pwntechnologies.com) and, hence, optimum sorption kinetics and reduced contact times. This can be done with any resin that is commercially available, and the resins used to date can be treated with hydroxide for biofilm control, if necessary.

The SIX®-process

Basic principle

In the SIX® process, resin is dosed from a dosing tank into the raw water at a low concentration of 4 to 20 mL resin/L, depending on the raw water quality, desired treated water quality, and resin type. This mixture then flows through plug flow contactors. In these contactors, the resin has the same residence time as the treated water, because the resin travels together with the water through these contactors. Unlike packed bed systems, in which the resin is retained in the contactors, all resin particles are exposed to equal conditions, leading to homogeneous distribution of the adsorbed matter over these particles. This, in turn, gives rise to a more stable and superior process performance, as well as more efficient use of the counter anion (Cl⁻) during regeneration.

The number, shape, and design of the contactors play an important role in the adsorption kinetics of this process. The aim of design is to approach the ideal contactor system of a plug-flow reactor [Ramaswamy, 1995], leading to shorter residence times of the resin, and therefore shorter contact times. After the contact time in the contactors, the resin is separated from the treated water using a customized lamella settler. The resin collects in the hopper, and is then immediately regenerated and returned to the dosing tank (figure 2).

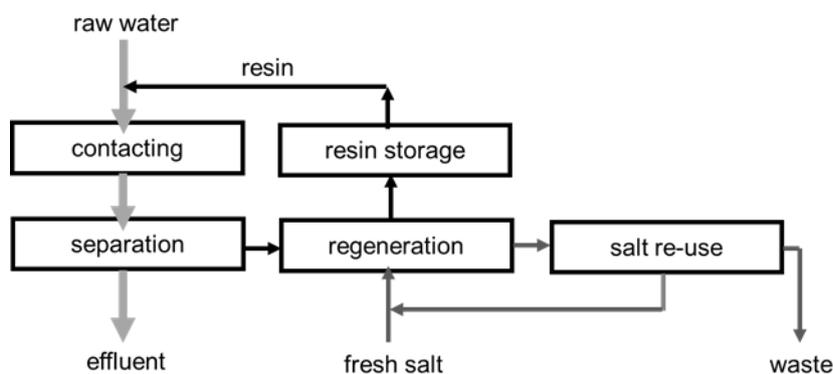


Figure 2, Schematic of the SIX® process of PWN Technologies

Kinetics

Knowing the exact residence time of the resin makes it possible to regenerate all of the resin equally, leading to an equally low number of regenerations for all of the resin. The relatively short contact time (e.g., 10 min < t < 30 min) of the treated water with the resin before the regeneration procedure makes it difficult and almost impossible for bacteria to grow on the resin particles surface. This overcomes the problem of resin blinding and ensures that the resin continues to operate at stable adsorption kinetics. This is shown with the help of a pseudo first-order reaction according to Lagergren, for which reaction constants can be determined using jar tests (Koreman 2013). According to this pseudo-first order reaction non equilibrium adsorption is controlled by an adsorption rate constant k (min⁻¹) and the difference between actual and equilibrium concentration. Since k is proportional with resin

concentration, normalization with concentration results in a constant value, the normalized rate constant K (L/min.mL resin)

First, the resin in this case the standard MIEX resin, has been loaded with the estimated amount of BV with the same raw water (in this case, raw IJssel Lake water). After that, a certain amount of this resin (i.e., 2,4, 8, 12 and 30 ml/L) of this resin were added to jars and regularly sampled to determine UV254nm Transmission (UVT) at various time intervals, ranging from 2 to 30 minutes. From the reactions, k values as a function of the resin concentration where determined. Table 15.1 gives the overall inventory of the different processes.

Table 1, Parameters and K-values of different processes for MIEX® resin

	SIX	MIEX classic	MIEX high-rate	FIX	Column
BV					
Min	50	200	2000	60000	12000
Max	250	1000	5000	120000	
Residence time resin					
Min (min)	10	300	>3000	>4000	>20000
Max (min)	30	600			
Average K-value	0.0419	0.0252	<0.0041	n calc	n calc

n calc = not calculated

The lower K-value of the classic MIEX® process compared to SIX® at almost the same BV of treated water immediately confirms that resin blinding not only with biomass but also with non-desorbed anions lowering equilibrium values as well as rate constants, occurs in the MIEX® process on this resin, with this feed water, at longer resin residence times. Using this K-factor to model UVT development in time for a certain resin concentration and initial UVT (UVT of the raw water) results in figure 2 , showing even more clearly the advantage of a single pass, leading to lower contact times or lower resin concentrations to reach a certain target UVT . Extending the BV and residence time further leads to a significant loss of adsorption capacity (i.e., lower k value and UVTeq), due to resin exhaustion and inadequate regeneration. With longer residence times and higher BVs of water treated before regeneration, it is easy to see that fluidized bed systems (FIX), and fixed bed columns are technically not feasible for treating this type of water. Resin blinding (biomass, residual adsorbed anions) undoubtedly occurs, and performance deteriorates. Finally, resin exhaustion gives rise to higher initial salt levels in the regenerant liquid, needed to maintain enough desorption efficiency and to prevent further deterioration of the adsorption capacity on the long term.

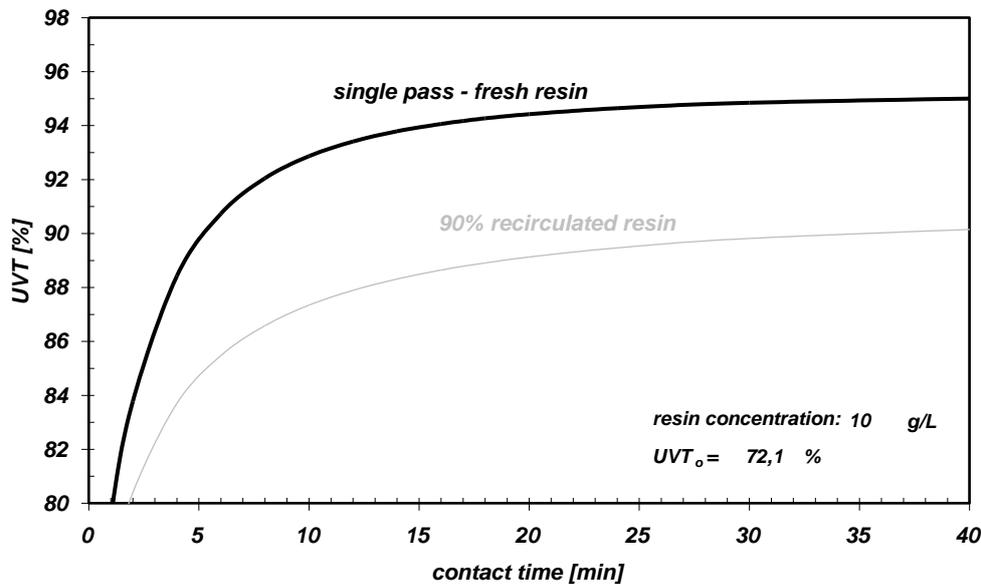


Figure 2, Modelling UVT development in time based on pseudo first-order reaction

Resin choice

The MIEX-resin itself has very high kinetics based on the same K-factor when fresh resin is used compared to other commercially available resins comparing them in ml/L (figure 3) . This is partly caused by the macro-porous properties and strong basic groups but mainly by its fine particle distribution creating a very large surface area compared to other macro-porous resins. Figure 3 shows that the adsorption kinetics differ from one resin to the other as was investigated by lab scale batch experiments. If resin choice would only be determined by these results, it would be difficult to explain why finally Lewatit VPOC 1017 was finally selected as the most preferred resin for Andijk III. The reason for this is that - next to adsorption kinetics - desorption kinetics, capital costs, resin debris and sedimentation properties are very important criteria too. With respect to the latter, Lewatit VPOC performs better than the other resins that were investigated. VPOC – a strongly basic acrylic gelular anion resin - has superior sedimentation properties and thus lamella separator footprint is relatively small, whilst the resin beads are less sensitive for abrasive (mechanical) forces and as a consequence fine particles “carry over” is very low. Further, its pore structure tends to be more of a macroporous type, rather than a microporous. As a consequence it contains less functional groups per unit surface area compared to the other resins that were investigated. This implies that relatively higher resin dosages need to be applied to achieve target UVT (DOC) levels, but on the other hand less salt and shorter desorption times are required during resin regeneration. Together with relatively low resin cost per unit mass, last mentioned benefit is of major importance for total cost reduction.

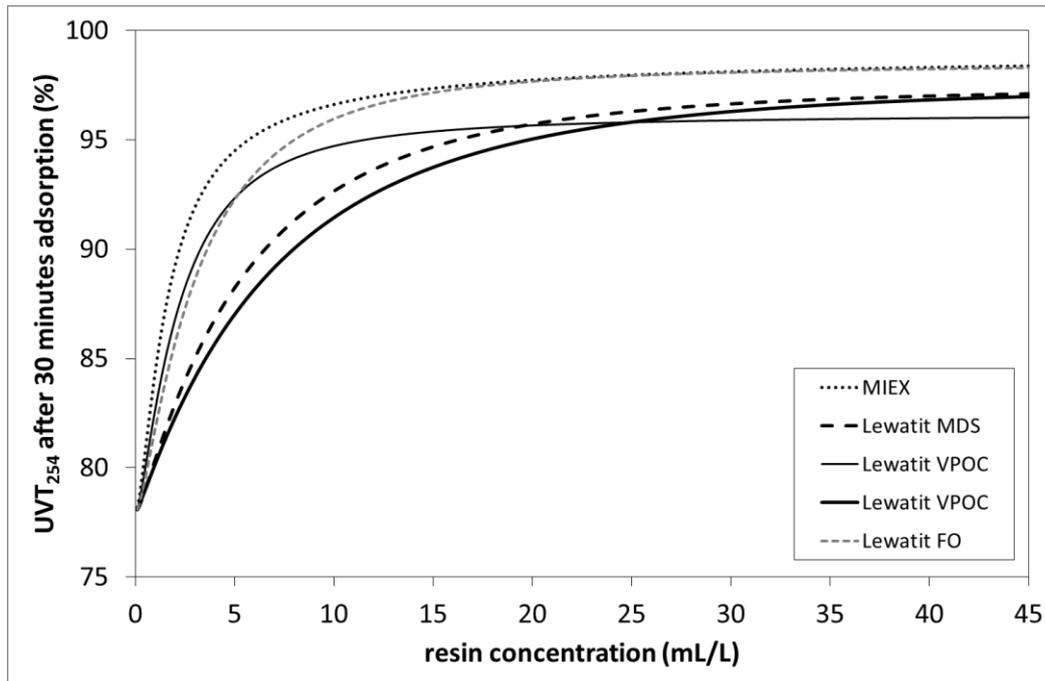


Figure 3. UVT₂₅₄nm for various anion exchange resins after 30 minutes adsorption as a function of resin concentration (raw water source: IJssel Lake)

Another advantage of this process is that because the resin is not fully loaded prior to a regeneration, the regeneration (equilibrium reaction) requires less salt and lower contact times for the regeneration procedure.

Case study WTP Andijk (PWN)

In 1920, when NV PWN Water Supply Company North Holland (PWN) was founded, the demand for drinking water was satisfied by ground water extraction. However, with the growing drinking water demand PWN was compelled to utilize surface water as an additional source. Therefore in 1968 Water Treatment Plant Andijk (WTP Andijk) was constructed for the direct production of drinking water from IJssel Lake (River Rhine). Originally the plant consisted of micro-straining, breakpoint chlorination, coagulation, sedimentation, rapid filtration and post disinfection (Figure 4). In 1978 the plant was upgraded with pseudo moving bed GAC filtration. In the beginning of the 90's a minor improvement in water quality was made by softening in the raw water reservoir by dosing NaOH in the intake from the IJssel Lake to the reservoir followed by a pH adjustment right before the micro-strainers with CO₂. After almost 40 years of operation, WTP Andijk still complied with all Dutch drinking water standards.

Nevertheless a second large upgrade was desired to install a universal barrier against pathogenic micro-organisms such as protozoa and organic micro pollutants such as pesticides [Kruithof, 2000]. This retrofit included the world's first large scale application of advanced oxidation with UV/H₂O₂ which became operational in 2004 [Kruithof, 2005]. This advanced oxidation is placed between the existing pre-treatment and GAC filtration (Figure 4). The GAC treatment provides removal of residual H₂O₂ and easily assimilable organic carbon (AOC). Since the advanced oxidation with UV/H₂O₂ requires a higher UV dose, superior disinfection is provided and breakpoint chlorination can be abandoned.

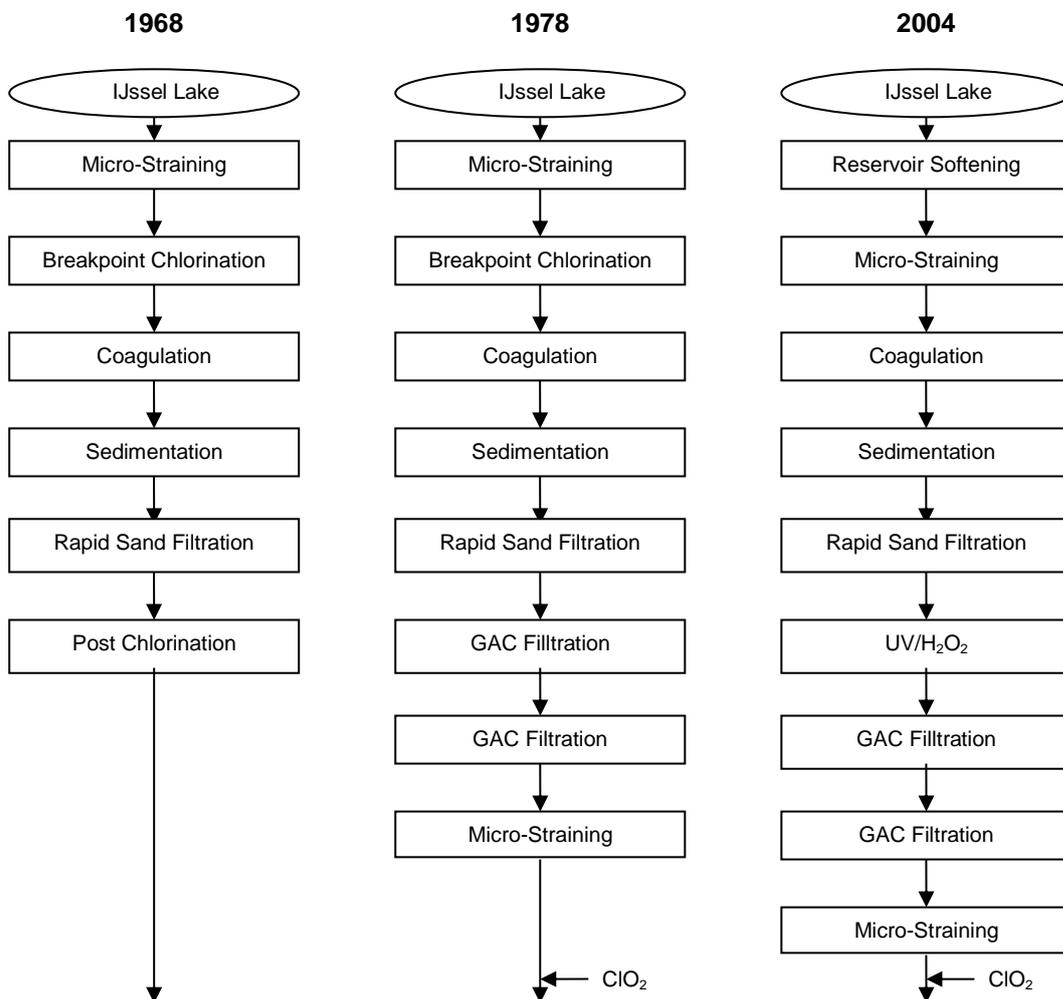


Figure 4: Technologic progression of WTP Andijk from 1968-2004

In a third phase the existing pre-treatment which still dates from 1968 will be renewed. The desire to retrofit the pre-treatment is based on a few challenges:

- increase the UV-transmission (UVT) to improve the efficiency of the advanced oxidation process (AOP);
- increase the removal of dissolved organic carbon (DOC) to improve the efficiency of the AOP and to lower the formation of AOC;
- remove nitrate to improve the efficiency of the AOP and to lower the formation of nitrite;
- total removal of suspended and colloidal matter independent of the feed water quality;
- increase overall capacity from 3000 to 5000 m³/h.

The wish to remove all suspended matter led quickly to the idea of using micro- or ultrafiltration (MF/UF). A former PWN study [Galjaard, 2005] indicated that the direct treatment of IJssel Lake water with MF/UF was only possible after the removal of the low molecular weight (LMW) DOC fractions with an anion resin (at that time MIEX®), which

resulted in a high gross flux rate with almost no fouling. The use of an anion resin like the also increased UVT considerably and removed a large amount of nitrate and DOC. The pre-treatment of ion exchange followed by MF/UF looked promising to fulfil the needs for the post-treatment and resulted in the first large scale SIX plant in operation since 2014.

Figure 5 represents seasonal fluctuations in raw water UV transmittance at 245 nm (UVT_{245}) and SIX effluent from the Andijk SIX pilot plant. During this period the pilot was operated at “regular” conditions, i.e. resin concentrations ranging between 13 and 15 mL/L and contact times between 25 and 30 minutes. These conditions were first selected as being the most appropriate for the Andijk situation by means of laboratory batch tests.

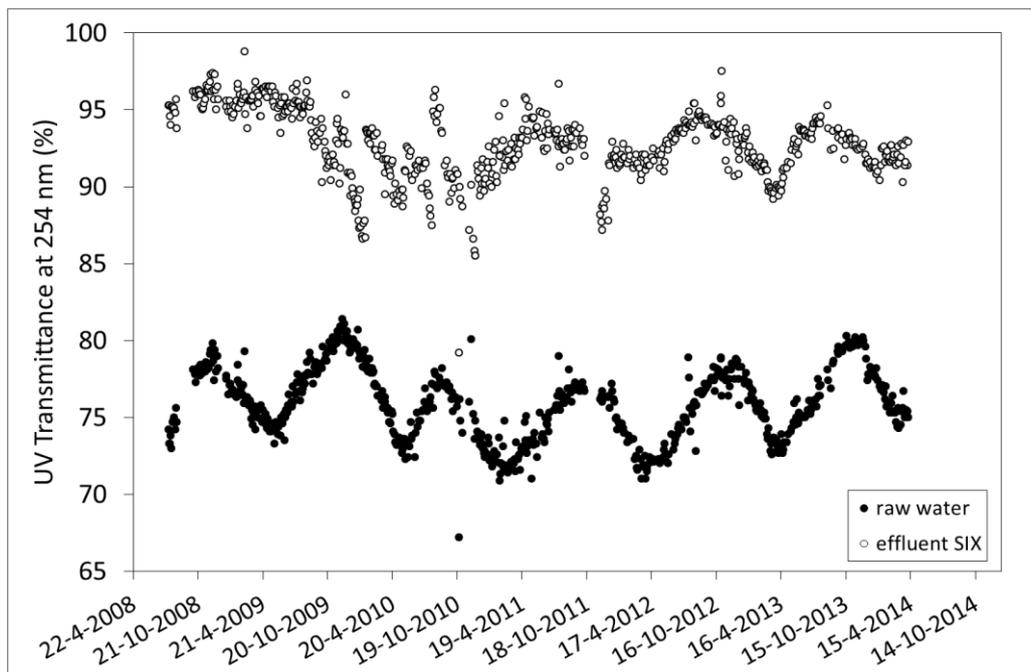


Figure 5. seasonal fluctuations in UVT_{254} for raw IJssel Lake water and Andijk SIX pilot effluent

One can see that raw water UVT_{254} has maximum values in late summer/early autumn. The opposite is true for the spring season. This has to do with fluctuations of the ratio between humic substances and biopolymers. This so-called HS/biopolymer ratio has a maximum value in the spring and a minimum value in late summer/early autumn. Since HS strongly adsorbs UV_{254} , whereas biopolymers do not (see figure 6). As a consequence, raw water UVT_{254} has the lowest values in spring, whereas DOC raw water levels do not fluctuate significantly over the whole season.

The difference between maximum and minimum UVT_{254} is quenched by SIX treatment. This is illustrated by figure 7 where we can see that the UVT increase is the highest in spring and summer and the lowest in the autumn and winter period. This can be explained by the fact that anion exchange in particular removes humics and (almost) no biopolymers, as has already been discussed. It also explains why we have better NOM removal kinetics in spring and summer since non equilibrium or rate limited adsorption is proportional with the difference between equilibrium UVT and initial UVT, as well as adsorption rate constant, that are both higher in spring and summer. Further quenching, if desired, can be obtained using higher resin concentrations during this period.

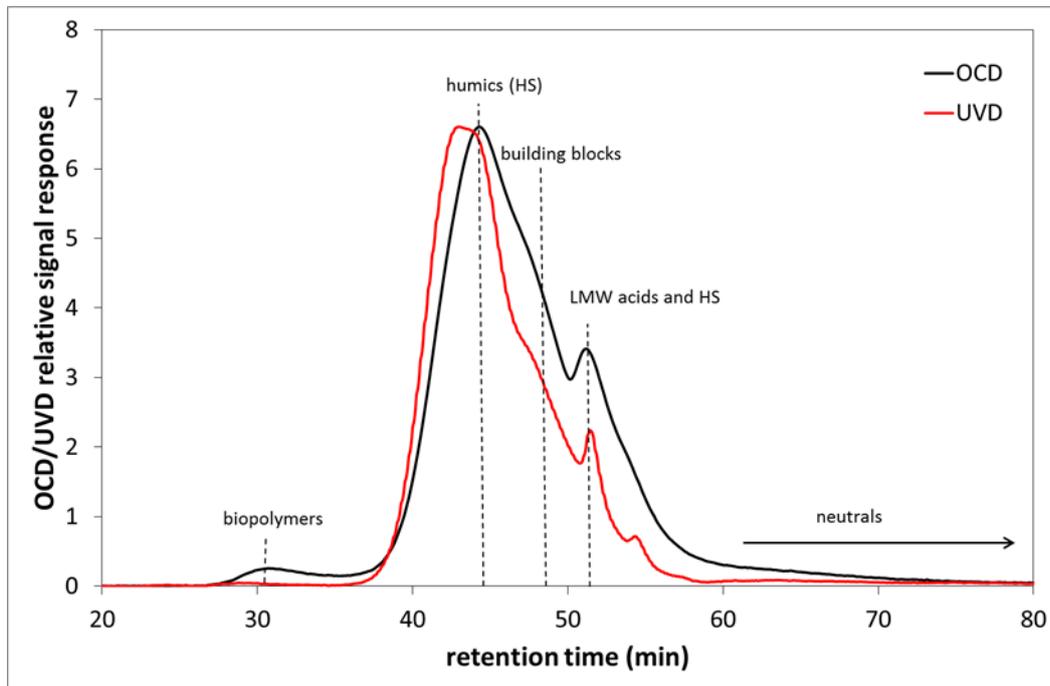


Figure 6. SEC-OCD/UVD spent regenerant chromatogram of SIX® treated IJssel Lake water

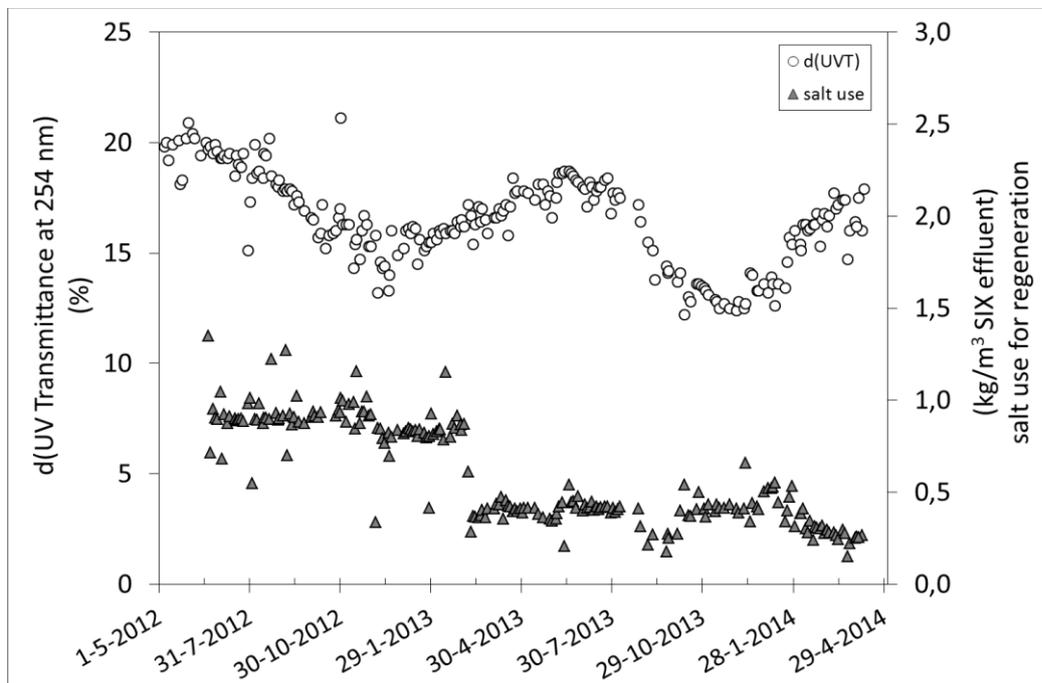
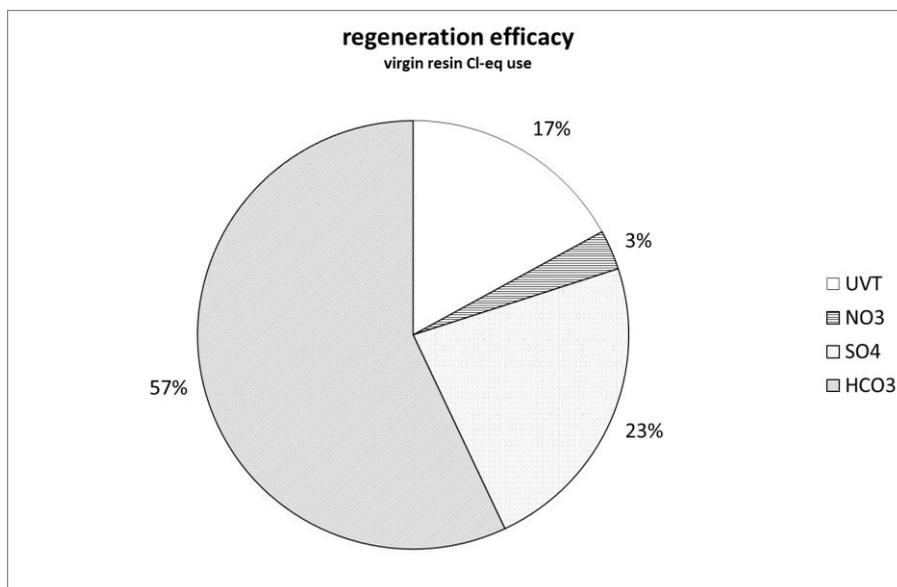


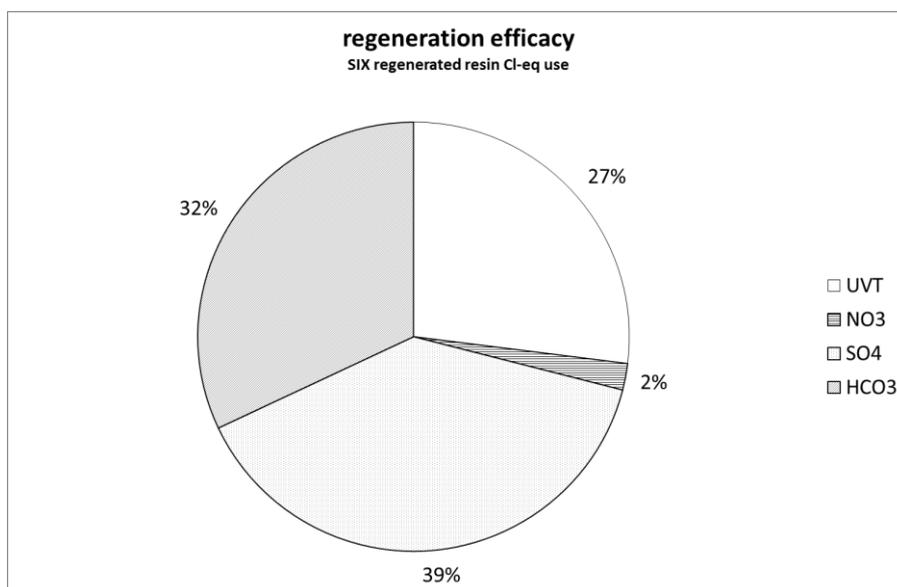
Figure 7. absolute UVT₂₅₄ improvement for Andijk SIX pilot treatment and salt use during regeneration

With respect to resin regeneration we may further state that a drastic reduction of the salt use had only little effect on UVT improvement, that seems to have been dropped with 1,0 to 1,5 %, after salt use was reduced with more than 65%. Figure 8 demonstrates why effluent-

UVT₂₅₄ - and thus NOM/DOC removal - is only slightly affected by this substantial reduction. Apparently, using (much) smaller amounts of chloride counter anions during regeneration predominantly results in blinding of adsorption sites for anions different from DOC. Since UVT₂₅₄ is an accurate surrogate parameter for DOC – for the Lake IJssel water matrix both are linear related with each other – comparison of both figures 8 a and b makes clear that reduction of the chloride use during regeneration has resulted in a higher chloride efficiency for UVT/DOC, i.e. the amount of chloride that is being exchanged with DOC during adsorption has increased with about 10% for the SIX regenerated resin compared with the virgin resin, mainly due to reduced HCO₃⁻ adsorption. The latter anion however is not a target anion, but rather a ‘chloride scavenger’.



(a)



(b)

Figure 8. comparison of virgin (a) and fresh (b) meq-chloride use efficiencies during anion exchange at 16 mL resin/L and 30 minutes contact time

Conclusions

Overall, the SIX-process functions really well and seems to be a solution for further removal of DOC. The higher removal of DOC but also other negatively charged ions impacts water quality and efficiency of all the downstream processes dramatically as was also demonstrated in Andijk and other locations among which Crownhill (South West Water) (Shorney-Darby, 2014). The advantages of SIX compared to existing ion exchange processes and enhanced coagulation/sand filtration systems (ECSF) are:

- no (significant) resin ‘blinding’;
- capable of using any available commercial resin;
- low resin concentration and inventory;
- high effluent quality;
- costs comparable or lower to ECSF.

With respect to regeneration we may conclude that:

- substantial reduction of chloride during regeneration of the loaded resins does not result in a noticeable deterioration of DOC removal per se. In Andijk it is first the bicarbonate anion adsorption that is being delayed, most likely because of its relative low position in the anion selectivity order. On the other hand DOC adsorption is only slightly retarded;
- Since chloride demand is being determined by total anion equivalents, SIX treatment becomes more attractive as the anion content – especially sulphate – is relative low.

With respect to the spent regenerant or brine we may further state that:

- The biggest risk for this process is brine discharge or treatment (0.2 – 0.4%), but this is a similar problem for a NF solution. The average salt usage for regeneration with no re-use is 0.05 – 0.2 kg/m³ treated based on the Andijk and Crownhill studies.

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