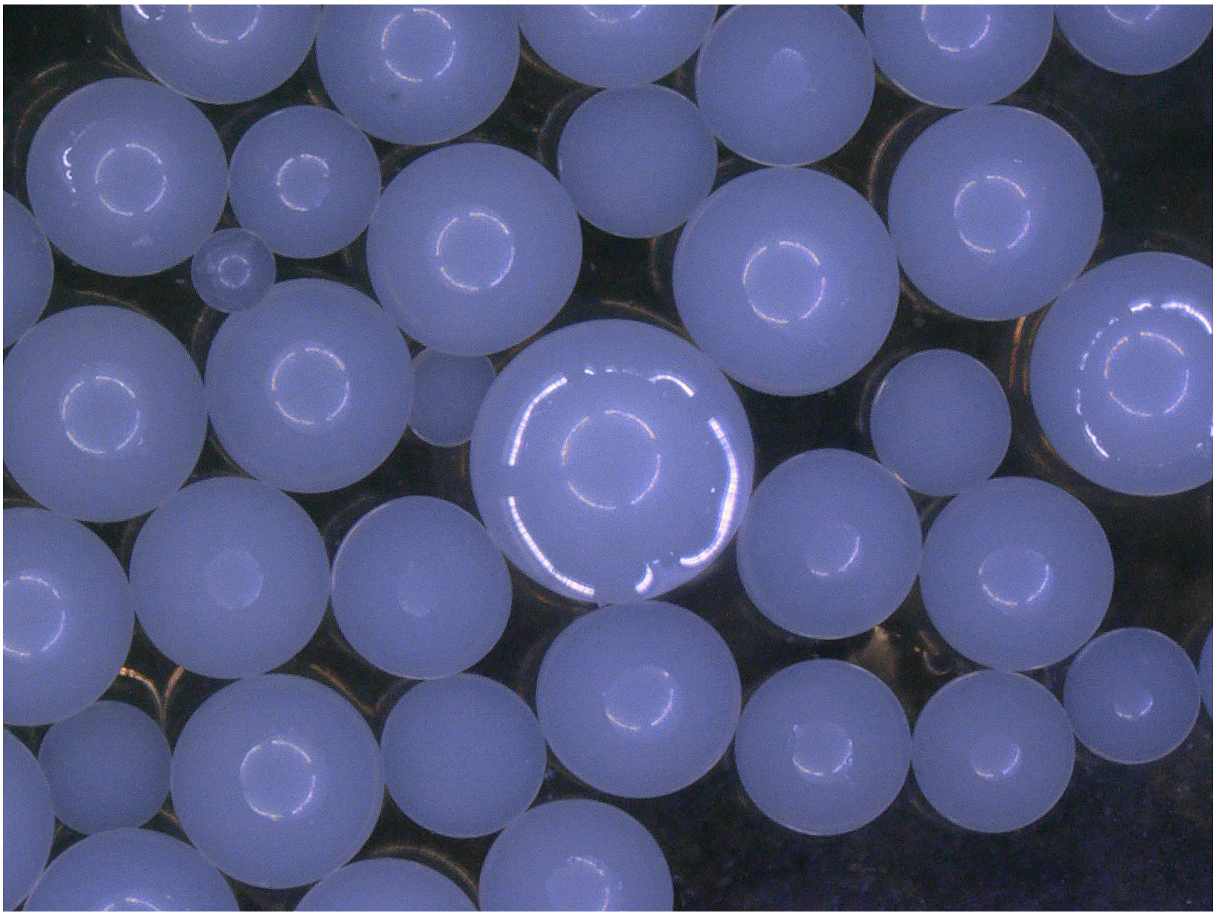
Predicting suspended ion exchange with PHREEQC



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Executive summary

Natural organic matter is one of the key components to remove from source water during drinking water production. NOM not only negatively influences the colour, taste and smell of the water, it also decreases the effectiveness of common water treatment steps such as (membrane) filtration and UV desinfectation. A big fraction of natural organic matter is negatively charged and because of that it can be removed from water with ion exchange.

Suspended ion exchange is a relatively new type of ion exchange, invented and developed by drinking water company PWN in the Netherlands. The trademark aspect of this process is that ion exchange resin gets dosed directly into the influent in suspension, followed by a filtration and a regeneration step instead of fixed bed reactors. The big advantage of this way of operating is that it can operate raw surface water, it is not prone to clogging and can operate continuously. Therefore it is much easier to implement towards the beginning of the water treatment chain, allowing it to positively impact later treatment steps.

PHREEQC is a computer program developed to do geochemical calculations. It is designed to take into account different chemical processes happening simultaneously in complex ground or water matrices.

This report is about the research done to see if the removal of natural organic matter through SIX can be simulated with a modeling program such as PHREEQC. Therefore a series of jar tests and titrations have been done to determine the relevant chemical properties of four different NOM samples, the influence of pH on ion exchange and the influence of competition between different target anions.

The counter anion exchange equivalence of NOM has shown to be varying from around 1.8 to 8. This can explain why it is observed that the adsorption of natural organic matter is almost unaffected by the presence of competing anions such as sulfate, as this high counter anion exchange equivalence suggests that NOM sits high in the anion selectivity range. Additionally, the adsorption of NOM has been constantly high over a wide pH range. This is remarkable, especially at low pH values where titrations show that the charge of NOM decrease drastically. The release of chloride by the resin does get affected by pH a lot however, although this is minimally related to the changing charge of NOM and rather by the increasing amount of bicarbonate in the system adsorbing to the resin at neutral or high pH ranges.

Using the equilibrium constants calculated with results from the jar tests in PHREEQC give quite accurate results when a system of two anions is simulated. When a system with more than two anions is introduced however, the program values the equilibrium constants too much, resulting in vastly underestimating the adsorption of whichever anion has the lower selectivity in the system.

NOM is currently too complex to accurately represent in a computer model compared to other, more common anions such as chloride, nitrate and sulfate. On top of that PHREEQC needs more parameters beyond exchange equilibria to properly model the exchange reactions in a model.

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List of abbreviations

DBP:	Disinfectant Byproducts
DOC:	Dissolved Organic Carbon
FEEM:	Fluorescence Excitation Emission Matrix
FIX:	Fluidized Ion Exchange
GPC:	Gel Permeation Column
IEX:	Ion Exchange
LC-OCD:	Liquid Chromatography – Organic Carbon Detection
LMW:	Low Molecular Weight
MIX/MIEX:	Magnetic Ion Exchange
NOM:	Natural Organic Matter
SIX:	Suspended Ion Exchange
TOC:	Total Organic Carbon
UVA:	UV-Absorbance, or: Ultra Violet light Absorbance
UVT:	UV-Transmission, or: Ultra Violet light Transmission

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1. Introduction

1.1 Natural organic matter removal through ion exchange

1.1.1 Natural organic matter

Origins

Natural organic matter (NOM) is a collection of natural organic compounds in water. It originates from the degradation of the remains of all types of organisms, such as plants and animals, and their waste products. Due to the common presence of said organisms in all types of environments, raw water sources will always contain an amount of NOM that requires treatment during a drinking water purification process (H. Dayarathne et al., 2021). However, not all organic compounds in natural waters have a natural origin and have rather anthropogenic roots (J.Lee et al., 2019). Lake Ijssel for example, contains water from the river Rhine, where various types of industry discharge their effluent and waste into. The industrial and agricultural contaminants are not to be confused with NOM as this consists only of natural compounds.

Effects on drinking water production

The natural organic matter in water treatment plants has negative effects on the water quality and the water treatment system itself. It influences the taste, colour and odor of the water and reacts with common disinfectants such as chlorine to form disinfectant by products (DBP) (Kaeocha, 2008). Also it can lead to a decrease in dissolved oxygen (A.Bathnagar and M. Sillanpää, 2017) and it decreases the transmission of UV light making disinfection harder and more resource consuming. NOM will also promote bacterial growth and can cause competition in activated carbon filters and fouling in membranes or other types of filters. For these reasons the control of organic matter is considered a key part of drinking water treatment and distribution.

Measuring methods

So far characterization of natural organic matter is proven to be troublesome because of the complex and diverse structure of NOM. It consists of hundreds of different molecules in various sizes and (low) concentrations. It has no guaranteed chemical properties, making it hard to analyze and unpredictable to work with (T. Reemtsma, 2009). There are some techniques that can fractionate and characterize the components to a limited extent. One of them is Liquid Chromatography – Organic Carbon Detection (LC-OCD). This method distinguishes molecules based on size, ion interaction and hydrophobia. With this method the sample is pumped into a column where molecules are separated based on their size in a gel permeation column (GPC), next a thin film of eluent is being created in a reactor which is being

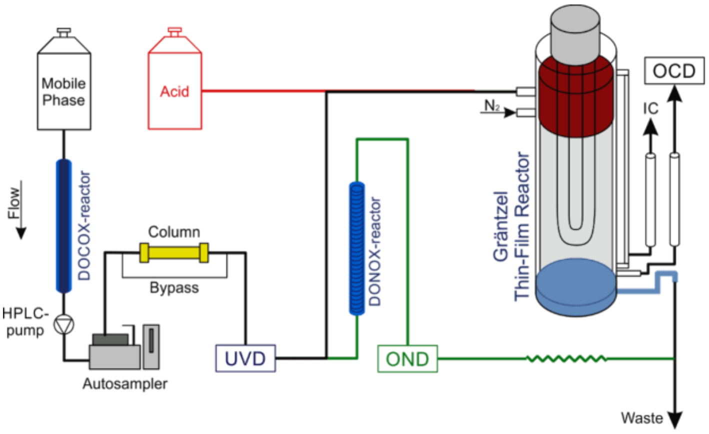


Figure 1: Schematic overview LC-OCD (www.doc-labor.de)

radiated with UV-light. This instantaneously turns the organic matter in CO_2 which can be measured with an infrared-detector (DOC-Labor homepage). LC-OCD divides NOM into different fractions (biopolymers, humic substances, building blocks, low molecular weight neutrals and acids) based on their molecular weights. Humic substances will be the most relevant fraction to this report as is explained in the next paragraph.

The figure below shows an example of how the results of a LC-OCD analyzation may look like. In this case the NOM was checked in particular for its humics and biopolymers fractions since they were the main targets of flocculation by adding $FeCl_3$

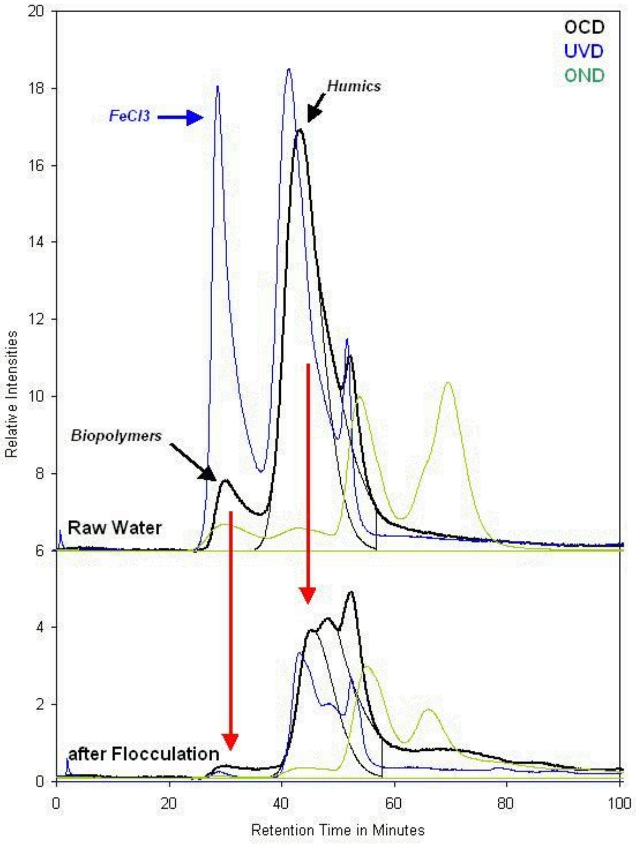


Figure 2: LC-OCD of raw water before and after flocculation (DOC-Labor website, application example of the inpact of flocculation on NOM, http://doc-labor.de/?page_id=253)

Another way to determine NOM fractions is using a Fluorescence Excitation Emission Matrix (FEEM). By measuring emitted radiaton intensity values as results of exicitation for different wavelengths. Based on the colour patterns in the matrix the NOM fractions and quantities can be determined. (J. Croft, 2012)

Natural organic matter is sometimes expressed as Dissolved Organic Carbon (DOC) and Total Organic Carbon (TOC). These parameters are less complicated and less costly to analyze and therefore used as a representative for NOM as a group parameter. DOC is defined as the concentration of dissolved organic carbon in water smaller than 0.45 µm (Kolka, Weishampel, Fröberg, 2008). TOC is all the organic carbon dispersed in the water without filtration and contains also cells and cell fragments. Therefore TOC will always be equal to or greater than the DOC.

Humic substances

This report will mainly focus on the ‘humic substances’ fraction of NOM (HS in the LC-OCD). Humic substances decrease the UV transmission (UVT) (J. Hur, 2011) and therefore make the advanced oxidation step (UV/H_2O_2) less efficient and more energy consuming. They are also responsible for the colour of the surface water (M. Klavins, M. Babre, 2002) and most of the physical and chemical properties of the NOM. This HS fraction has shown to be 30% to 90% removable by ion exchange (I. Luvchuck et al, 2018) and this has therefore further been developed by PWNT in the SIX technology.

The humic substances fraction of NOM in (surface) waters can generally be distinguished into two main fractions itself too: humic acids (HA) and fulvic acids (FA). Since HA are insoluble at extremely low pH values they can be separated from FA by lowering the pH to close to 1 so they will precipitate. (IHSS website)

Removal of humic substances from water

As mentioned in the previous paragraph one way to remove humic substances from water is through pH adjusting. This can be an expensive method, especially if such changes are required to be reverted further down the drinking water purification stage. Therefore in practice natural organic matter usually get removed by using the fact that humic substances are negatively charged. Using this chemical property a drinking water company can opt for sedimentation/flotation, filtration (sand or membranes such as nanofiltration or reverse osmosis membranes), ion exchange or the combination of coagulation/ filtration and biological treatment. (Y. Zhang et al, 2015) This report will focus on removal of NOM through ion exchange, suspended ion exchange in particular.

1.1.2 Ion exchange

Ion Exchange

Ion exchange is a technique used in water purification, in which charged compounds are being separated from water by electrostatic interaction. These target compounds are dissolved and therefore not filterable. To be able to separate these compounds with ion exchange, it is required that they are either positively charged (cations) or negatively charged (anions). The exchange is usually done using ion exchange resins. These are small, porous polymer-beads containing charged functional groups and mobile ions of the opposite charge to maintain electric neutrality. When added to the water in sufficient concentrations the mobile ions will exchange with charged compounds in the water that have the same charge. For this reason an ion exchange resin can only remove either anions or cations. It is important that there is a difference in affinity of the resin for the mobile ions on the resin and the ions that are to be removed from the water. The resin should have a higher affinity for the ions in the solution than for the mobile ions on the resin. Most of the time multivalent ions have a higher affinity compared to monovalent ions, therefore the mobile ions are always monovalent, Na^+ or Cl^- are common ions used on resin. (Dupont website)

Different types of ion exchange

Usually the water with the target ions (influent) is continuously led through a fixed bed reactor with resin until the resin is considered exhausted, which is when the effluent of the reactor contains more than the maximum amount of target ions. As soon as this threshold is reached, the resins get backwashed to start regeneration. Regeneration of resins is making use of the reversibility of the ion exchange process by washing the resins with high concentrations of salt, made up of the mobile ion exchange ions (counter ions). Because of the higher affinity of the resins for target ions than the original ions on the resin, an overdose of counter ions is required to push the equilibrium ion composition of the resin towards the original state. After regeneration the resins are ready for another cycle of ion exchange while the counter ions are removed as a saline waste brine, sometimes called 'spent' regenerant.

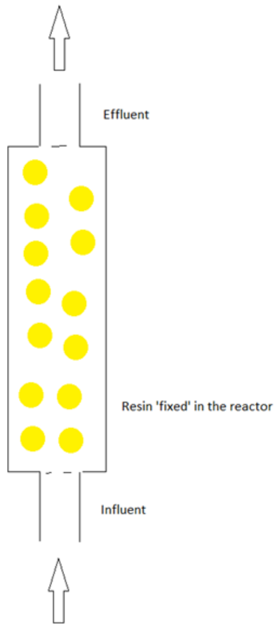


Figure 3: Schematic overview fixed bed reactor

In recent ion exchange history the research focus has been on more continuous processes without the clogging problem of a packed bed and the advantage of using this towards the beginning of the treatment train. This has led to various newer types of ion exchange processes such as the following (D. Metcalfe et al., 2015):

- Magnetic Ion Exchange (MIEX)
- Fluidized bed Ion Exchange (FIX)
- Suspended Ion Exchange (SIX)

MIEX

Magnetic Ion Exchange uses special types of resin that have magnetic properties so the small beads coagulate spontaneously and are easy separated from the water after the ion exchange process has ended. Currently those resins are used to separate remove NOM from water. (K. Cadee, 2001)

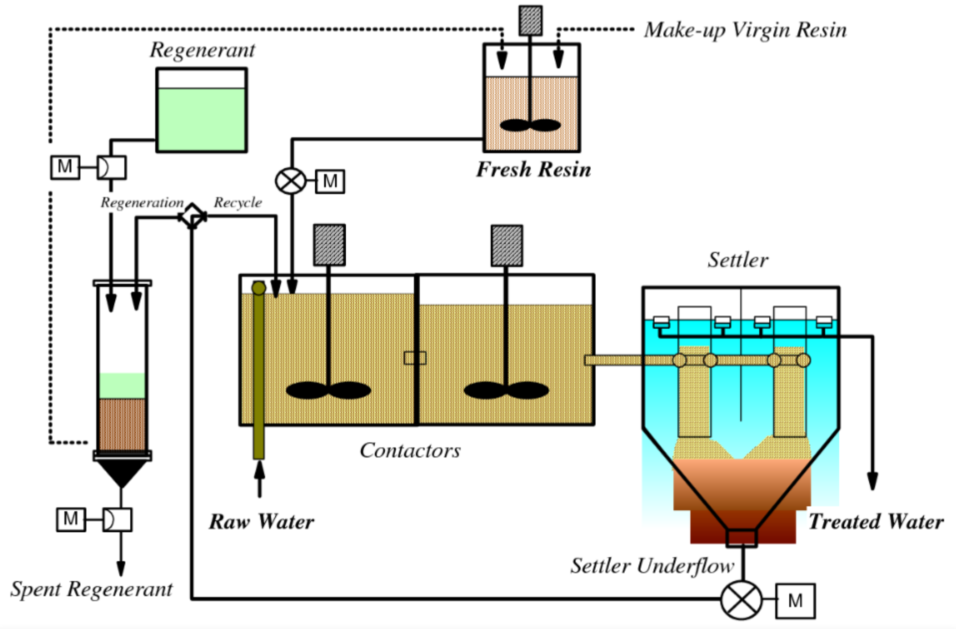


Figure 4: Schematic overview of MIEX reactor (K. Cadee, 2001)

FIX

Fluidized bed Ion Exchange is similar to a regular fixed bed system with the main difference that the target anions are removed by anions in a fluid that is loaded with upflow. The big advantage of this system is that clogging is not possible. (M. Kalaruban et al., 2016)

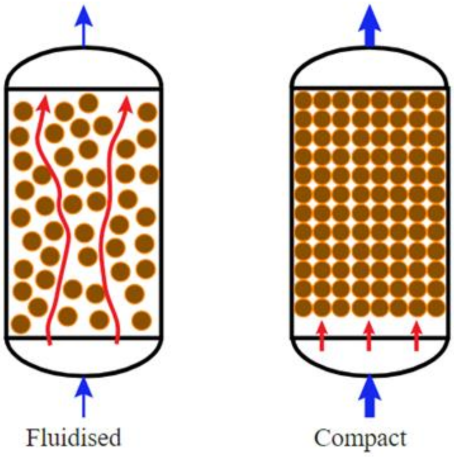


Figure 5: Schematic overview of fluidised bed IEX compared with a packed bed column (http://dardel.info/IX/processes/columns.html)

SIX

Suspended Ion Exchange is a newer ion exchange method where the resin is freely suspended in the treated water and later filtered out again. This method combines the advantages of a continuous process and lack of clogging of processes happening in and after SIX. (PWNT website)

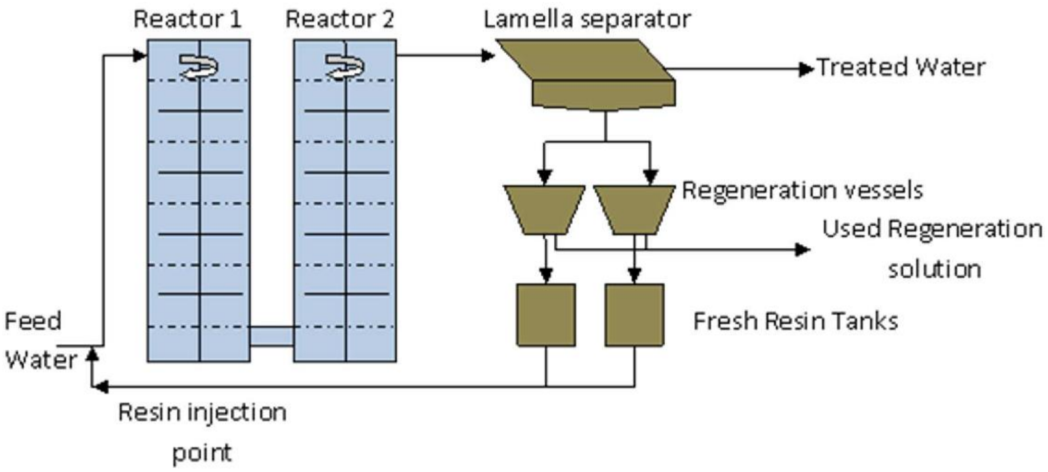


Figure 6: Schematic overview of SIX (J. Im, 2015)

Ion exchange resin properties

Some of the most relevant properties of ion exchange resins are the following: (Wachinski, 2006):

- Capacity: The exchange capacity is an indication for the amount of ion equivalents that can be exchanged. Often expressed as equivalents per liter (eq/L), the amount of mobile exchange ions desorbed should be equal to the eq of ions adsorbed, whether these are the target ions or not.
- Bead size: The size of the resin beads influences adsorption and desorption kinetics. Smaller beads will have faster adsorption due to the larger surface are where ion exchange can happen. Also the resistance of a packed bed is influenced by the bead size as well as the sedimentation velocity (which is important for the SIX concept)
- Selectivity: The various charged molecules will compete for places on the resin. In general ions with a higher valence and greater atomic weight have a higher affinity for ion exchange resins.
- Ability to regenerate: The quality of resin that has been regenerated multiple times is usually decreasing since not all exchanged ions will be washed away by the counter ions. This depends on the concentrations used in the exchange reactor (target ion and resin concentrations) and in the regenerators (counter ion concentration and loading of the resins), the amount of resin fouling by non-target molecules and the selectivity of the resins.
- Porosity: The porosity of the resins has major influence on the previous two properties. The amount, the size and the depth of the pores determines how efficient and how fast exchange takes place. The rate of ion exchange and regeneration depends on the amount of diffusion in the respective reactors, therefore small or deep pores (micro-porous) are unfavorable. Macro-porous resins have larger pores and as a result will have less total exchange surface. The advantage of these resins are easier regenerabilty.

Suspended Anion Exchange (SIX)

Suspended Ion Exchange (SIX) is a relatively new type of ion exchange treatment, developed by PWN, a drinking water company from the Netherlands . In contrast to classic ion exchange systems needing operational interruptions to backwash the resins, SIX keeps the resin in suspension with the water, functioning as a plug flow reactor, followed by sedimentation in a lamella separator. The big advantage of SIX over a classic packed bed ion exchange systems is that it can be used earlier in the treatment plant, where packed bed systems cannot do this since they will suffer from fast clogging. This also means that the rest of the treatment plant will benefit from the early removal of NOM and anions. SIX also separates itself from other newer ion exchange methods with minimal clogging such as fluidized bed ion exchange (FIX) and magnetic ion exchange (MIEX) by also having the advantage of a continuous system as no backwashing is needed and that a much lower resin concentration and contact time can be used. The continuous system not only is an advantage because there is no downtime needed for backwashing, but also prevents resin blinding which can happen if resin is in the reactor for extended periods of time to minimize the amount of regeneration cycles (E. Koreman, G. Galjaar, 2016). This resin blinding of active groups on the resin is caused by bacteria that can feed on phosphorous and carbon groups on the resin and results in the need for higher resin concentrations and contact time.

Resin is added just before the entrance of the water in 5 reactor tanks, which are connected in series. This is to keep the mixture in the reactor as homogeneous as possible, leading to a more uniform contact time distribution (a low derivation from the hydraulic residence time), lower required resin concentration, an equal loading of the resin compounds and the availability to treat waters with high concentrations of suspended solids. Because of these beneficial circumstances the resin is not being loaded with target ions until exhaustion and therefore it is easier to regenerate the resin to its original state later in the system. The shorter contact time is determined experimentally to be 30 minutes, which is short enough to prevent bacterial growth, which in turn prevents resin blinding and reduces fouling in the downstream Ceramac process (Koreman, Galjaard, 2016).

After those 30 minutes the suspension is led to the lamella separators. They easily separate resin from water, due to the favorable sedimentation property of the resin compounds. This makes a high hydraulic load (6-10 m3/h.m2 projected lamella surface) possible, leading to a smaller required footprint of the lamella separators. From time to time the ‘hoppers’ underneath the lamella containing the separated resin are being drained and discharged to the regeneration vessels.

The water is led to the next step in the treatment plant, which are the Ceramac membranes in the case of Andijk III. The separated resin is stored in regeneration vessels where water with high salt NaCl concentrations (20-30 g/L) (Im, Koreman, Malley, 2015) is added to initiate the regeneration process, restoring the amount of chloride ions on the resin beads. Because of the lower exchange loading of the resin compared with classic ion exchange systems, less counter ions and therefore less chloride is required to restore the resin in its original state and a high regeneration efficiency is obtained.

The regenerated resin is then stored in dosing tanks, ready for a new cycle of ion exchange. The salt used to regenerate the resin is being used 5 times before it is being disposed. This strategy strongly reduces the amount of salt used. After each regeneration cycle, instead of pumping the salt into a large container, the regeneration salt is stored separately, depending on how often the regenerant has been used. Each regeneration starts with a 4 times used regenerant, followed subsequently by 3 times used, 2 times used, 1 time used and fresh salt.). After five cycles the amount of chloride in the regeneration brine is approximately a third of the original concentration, meaning a third of the chloride in the salt is used to remove anions from the resin during the regeneration process. The remaining regeneration fluid is discharged as a waste stream. There is still ongoing research to reuse the spent regenerant, also referred to as brine. The brine from the regeneration vessels contains high concentrations of sodium, chloride, sulfate, phosphate, nitrate and NOM and the disposal and/or reuse of this brine is currently one of the biggest challenges in the application of ion exchange treatment in drinking water production.

After performing experiments by doing jar tests and bench scale tests focused on the DOC removal and regeneration qualities of various anion exchange resins Andijk III have chosen to use the Lewatit S5128 resin in a concentration of 15 g/L in their SIX system (Koreman, Galjaard, 2016). This is a micro porous gel type strong base resin with type 1 quaternary ammonium groups combining decent DOC removal with sufficient regenerability.

1.1.3 Andijk III drinking water treatment plant

PWN is the main drinking water supplier in the majority of the province of North-Holland in the Netherlands. It has multiple treatment plants, located in Andijk, Bergen, Heemskerk and Wijk aan Zee. The Andijk III treatment plant is located in Andijk, its location is shown in figure 7 to the right. At Andijk also PWN's daughter enterprise PWN Technologies (PWNT) is situated. This is the Research and Development team developing new technologies in water treatment, such as SIX and CeraMac, which are implemented at Andijk III.

Figure 7: Water delivery area for PWN with the location of Andijk III and its delivery area in orange (www.pwn.nl)

At Andijk III the water source is Lake Ijssel. Due to the size of the lake the residence time of the water is high enough so that most compounds can settle to the bottom before reaching the intake point.

This water will then be stored at reservoirs where it is softened by adding caustic soda to form calciumcarbonate ($CaCO_3$). The water remains in the reservoir for approximately 9 weeks to minimize fluctuations in the water quality in the downstream treatment process and to settle the $CaCO_3$ that precipitates after adding NaOH.

The water from the reservoirs is pumped into the treatment plant through sets of drum screens as an initial filter to block particles larger than 0.2 mm, such as algae. This softened and filtered water is the SIX influent. SIX removes most negatively charged ions (see also next chapter) using anion exchange resin. Only exception is chloride as this anion will increase in concentration due to it being the counter anion used to replace the target anions in the water.

The SIX effluent receives a combination of UV-light treatment hydrogen peroxide (H_2O_2) dose to remove micro-pollutants, such as pesticides, herbicides, fungisides, pharmaceuticals and bacteria. This combination of UV and H_2O_2 is called advanced oxidation, which is then followed by the CeraMac membranes. These membranes remove further suspended matter and bacteria remains.

Any remaining pollutants and peroxide in the water are then removed by granular activated carbon (GAC). Here the hydrogen peroxide is turned into water and oxygen and gets biological treatment to remove any other advanced oxidation treatment leftovers. Finally the water is stored and distributed to PWN customers.

1.2 Problem definitions

This report will focus on researching the possibilities of creating a program that can give a reliable first indication of the performance of SIX, especially regarding NOM adsorption. This can be beneficial to potential SIX clients as they can obtain a global indication of the performance in an easy manner before investing much time and money into other research. This model will also be a helpful tool during future research and development projects as some parameters (such as bicarbonate and NOM) are relatively hard to measure. The program used is PHREEQC, a water chemistry program that is usually used for groundwater calculations that has all the tools required for creating a model for simulating ion exchange adsorbing NOM from surface water.

To decide whether modeling SIX and NOM adsorption is practical the following research question and sub questions will have to be answered:

Is it possible to predict the IEX performance for various pH values based on the anion composition of the influent with PHREEQC?

- *1. What are the ion exchange properties of NOM and how do they compare to other anions?*
- *2. How does pH influence NOM and anion concentrations during SIX?*
- *3. How do the resin concentration and competition between anions influence NOM and anion adsorption during SIX?*

Goal: to make a computer model that can predict IEX performance (SIX in this case) based on the anion concentrations in the influent, the pH and the resin dosage.

2. Theory

To simulate ion exchange in a computer model, more in depth knowledge on ion exchange and NOM is required. This chapter will look into some fundamental aspects of these topics.

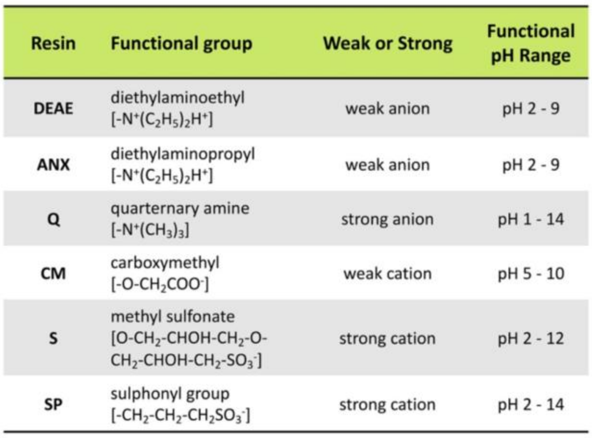
2.1 Ion exchange

Target and counter anions

Ion exchange basically consists of ion exchange resin being brought in contact with water containing target ions. The resin is loaded with counter-ions that get swapped with the target ions in the water. These counter-anions are either all positive or negative. Therefore a resin can only remove either positive or negative ions. By creating an environment with sufficient contact time, the resin gets loaded with target ions as much as possible until the ion exchange process approaches an equilibrium state. Then the resin and water are separated so the resin can be regenerated to be used again.

Resin types

Ion exchange resin consists of small polymer beads with charged groups. Those groups allow the resin to contain counter-ions that exchange with target ions. The type of reactive group determines what ions (cations or anions) can be removed with the resin and how easy it is for the resin to attract target ions for different pH values: strong acidic or basic resins can remove target ions on a broader pH range than weak acidic or basic resin. The advantage of weak acid or weak basic resins is that they can be regenerated either with an HCl or NaOH rather than with a salt. No overdose is needed in case of a weak acid or a weak basic resin in contrast with the large overdose of NaCl used to regenerate a strong acid or strong base resin. Also the capacity of a weak resin can be much higher than a strong IEX resin. Some common reactive groups on resins with their ion exchange qualities is shown in the table below:



Resin	Functional group	Weak or Strong	Functional pH Range
DEAE	diethylaminoethyl $[-N^+(C_2H_5)_2H^+]$	weak anion	pH 2 - 9
ANX	diethylaminopropyl $[-N^+(C_2H_5)_2H^+]$	weak anion	pH 2 - 9
Q	quarternary amine $[-N^+(CH_3)_3]$	strong anion	pH 1 - 14
CM	carboxymethyl $[-O-CH_2COO^-]$	weak cation	pH 5 - 10
S	methyl sulfonate $[O-CH_2-CHOH-CH_2-O-CH_2-CHOH-CH_2-SO_3^-]$	strong cation	pH 2 - 12
SP	sulphonyl group $[-CH_2-CH_2-CH_2SO_3^-]$	strong cation	pH 2 - 14

Figure 8: Several common ion exchange functional groups and their basic properties (E. McSweeny, 2017

The resin used for SIX is based on quaternary ammonium groups and is therefore a strong basic resin. A strong basic resin is able to remove target anions under a large pH-range.

Exchange reaction

An ion exchange reaction can roughly be described with the following equation:

$$C(adsorbed) + T(aq) \leftrightarrow T(adsorbed) + C(aq) \qquad (1)$$

Where:

- C: counter-ion
- T: target ion

The resin is loaded with counter-ions that swap places with target ions in the water. As can be seen from the equation, the reaction is reversible. This allows the resin to be cleared from the target ions and be restored in its original state with counter-ions. Figure 9 below shows a schematic example of this of anion exchange where with chloride as counter-ions (yellow) and target ions in red.

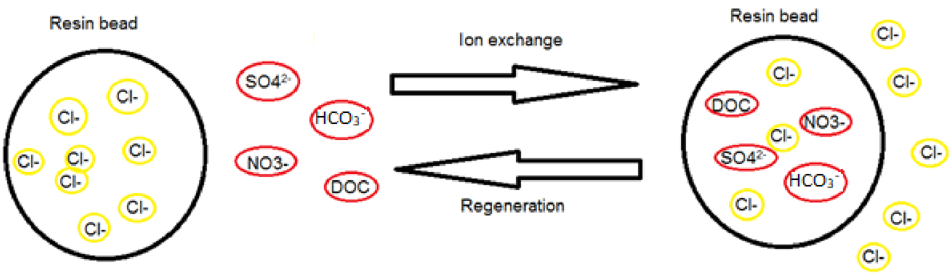


Figure 9: Schematic overview of anion exchange process in SIX

This example is a schematic overview of the SIX process at Andijk, which is the main ion exchange process studied in this report. Chloride is used as counter-anion to remove negatively charged DOC. During the exchange process DOC and other anions are being attached to the resin, while chloride is released into the water. During regeneration the resin, loaded with target ions, gets 'washed' in water with a high chloride concentration. The high concentrations of chloride will force the target ions off and replace the spots on the resin again so the resin can be reused for ion exchange. (*bron*)

Using those anions in the basic ion exchange equation (1) would result in:

$$R'(3+x)Cl^{-} + DOC^{x-} + SO4^{2-} + NO3^{-} \leftrightarrow R'(DOC^{x-} + SO4^{2-} + NO3^{-}) + (3+x)Cl^{-} \qquad (2)$$

In this example x is the average charge of DOC molecules.
In practice the reaction will never shift fully to the right or the left so in equilibrium all mentioned ions will appear both on the resin and in the water. The amount of each ion on the resin and in the water depends on an ion exchange property called selectivity.

Selectivity

Selectivity is an indication of the affinity between a certain ion exchange resin and the target ion. This property can be used to find a suitable resin for the removal of specific ions (T. Luo et al, 2020). For a strong base anion exchange resin the order of selectivity usually looks like this:

$S04^{-2} > I- > NO3^{-} > Cr04^{-2} > Br^{-} > Cl^{-} > OH^{-}$

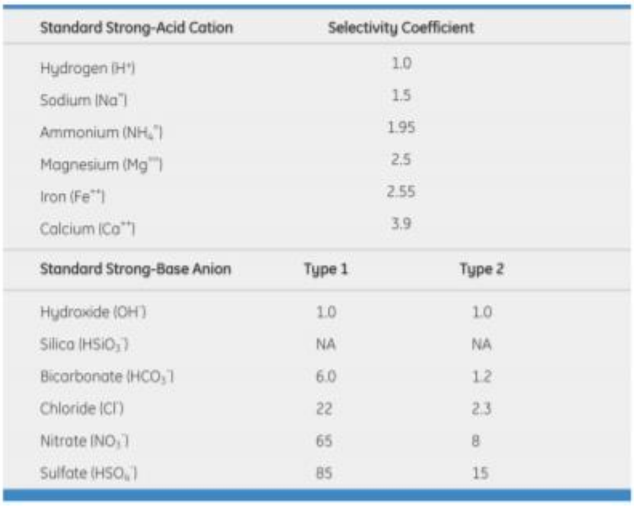
Then the selectivity between a resin and an ion can be roughly expressed with the equilibrium constant using a form of the following equation:

$$K = \frac{T(adsorbed) * C}{T * C(adsorbed)} \qquad (3)$$

Where:

- T is the target anion (mol/L)
- C is the counter anion (mol/L)

This shows that a higher K value means the resin is more likely to attract the target ions from the water and the counter-ion is released into the solution.
Some examples of selectivity values are given in the table below:



Standard Strong-Acid Cation	Selectivity Coefficient	
Hydrogen (H^+)	1.0	
Sodium (Na^+)	1.5	
Ammonium (NH_4^+)	1.95	
Magnesium (Mg^{++})	2.5	
Iron (Fe^{++})	2.55	
Calcium (Ca^{++})	3.9	
Standard Strong-Base Anion	**Type 1**	**Type 2**
Hydroxide (OH^-)	1.0	1.0
Silica ($HSiO_3^-$)	NA	NA
Bicarbonate (HCO_3^-)	6.0	1.2
Chloride (Cl^-)	22	2.3
Nitrate (NO_3^-)	65	8
Sulfate (HSO_4^-)	85	15

Figure 10: Selectivty values (compared with hydrogen/hydroxide) for common ions. Type 1 resins use a quaternized amine functional group, while type 2 relies more on the reaction of the styrene-DVB copolymer with dimethylethanolamine. This means type 2 is weaker base than type 1, but strong enough to not classify as a weak base resin. (Suez water technologies)

It should be noted that the actual removal of target ions depends on various factors such as their concentration, amount of competition of other ions, pH and temperature of the water (source) and that when an ion and a resin have a high affinity, this means regenerating the resin will be difficult and the counter ion should be overdosed.

Molar fraction

The equilibrium equation of the exchange between a target anion such as sulfate and a counter anion such as chloride is given below with the Z indicating the fraction of that anion that is adsorbed on the resin. If we fill this in into equation 3 we obtain:

$2ClZ + SO_4^{2-} <> SO_42Z + 2Cl^-$

Using Apello and Postma (2005), the anions in adsorbed state can be expressed using the molar fraction (β) where they are expressed as a fraction of the number of total exchange sites on the resin, like is done in 6.18a in Apello and Postma. This gives:

$$K = \frac{\beta_{SO4} * [Cl-]^2}{[SO4^{2-}] * \beta_{Cl}}$$

The β for a specific target anion can be determined with:

$$\beta_i = \frac{(\Delta C_i) * eq_i / d_i}{R} \qquad (4)$$

where:

- ΔC_i is the difference in concentration (adsorbed) of the target anion i (mg/L)
- eq_i is the counter anion exchange equivalent of anion i
- d_i is the molecular weight of anion i (g/mol)
- R is the amount of exchange locations on the resin (1.25 eq/L for Lewatit S5128)

Since each β is a fraction of the total amount of spots, this means that the sum of β's must be 1 and the β_{Cl-} can be determined by subtraction of the other fractions, the target anions m:

$B_{Cl-} = 1 - \Sigma\beta_m$

Where $\Sigma\beta_m$ is the sum of fractions of all ions besides counter anion Cl^-: the target anions.

Counter-ion equivalence

The counter-ion equivalence is showing the amount of counter-ions that exchange on average for a certain target ion. This means that a monovalent counter-ion exchanging with another monovalent ion will have a eq of 1 but this value will increase when the target ion is multivalent as for example one sulfate ion exchanges with 2 chloride ions on a resin with chloride as counter anion.

This number is useful to know since the amount of target ions on resin can only be determined by comparing the ion concentrations in water before and after ion exchange. The amount of counter-ions will obviously increase and using the equivalence value it can be determined which portion of the increased amount of counter-ions is responsible for the amount of decreased target ions.

Table 1: Equivalence values of most common anions in SIX

Chloride	1
Sulfate	2
Nitrate	1
Bicarbonate	1
Carbonate	2

2.2 NOM

Due to the fact that natural organic matter exists of numerous types of different molecules there is not a single set of chemical properties that can be accounted for a given NOM sample. This would require each sample of NOM and each of its individual molecules to be analyzed individually which would obviously become an unimaginable amount of work. Therefore the amount of NOM is often determined by measuring DOC (dissolved organic carbon) or TOC (total organic carbon) amounts, which are parameters that are relatively easy to measure. However, this only gives an impression of the NOM concentration in the water and does not add further information on the chemical properties of NOM (M. Edgar, H. Boyer, 2021). These qualities still mising include:

- Molecule size distribution
- Functional groups (polar groups, acid and base groups)
- Influence of water matrix on NOM molecules and their removal (such as pH or the presence of other ions)

2.2.1 Molecule size

The size of NOM molecules varies greatly. The order of magnitude of the molecular weight can be from around 100 D to tens of thousands D. There are several ways of measuring the sizes of NOM samples, but one of the most currently used ones is LC-OCD. As stated before, this methods distinguishes the following fractions (Y. Penru, 2013):

- Biopolymers (>20000 D)
- Humic substances (~1000 D)
- Building blocks (300-500 D)
- Low-molecular weight (LMW) neutrals (<350 D)
- LMW organic acids (<350 D)
- HOC (hydrophobic organic compounds)

Biopolymers are the fraction of NOM molecules that is largest in size. They are usually polysaccharides and amino sugars and are hydrophilic and are basically non-ionic meaning they can not be removed with ion exchange.

Humic substances (HS) are organic compounds that are based of humus and other organic remains. They have negatively charged groups (mainly carboxylic acids) at neutral pH and therefore make this fraction well removable by ion exchange. HS can be devided in three main fractions: humic acids, fulvic acids and humins. (E. Pettit, 2012)

Humic acids (HA) are a combination of aliphatic and aromatic organic acids that are soluble in water and precipitate only at the most acidic conditions. ($pH < 2$). They are usually large molecules (1000-100000 D) Recent studies by I. Caltran have shown that membranes can separate humic acids from fulvic acids at around 1000 D. Therefore in this report the molecular weight of humic acids will be assumed to be 1000 g/mol.

Fulvic acids (FA) are also a combination of aliphatic and aromatic organic acids but are soluble under all pH's. They are generally smaller than humic acids (around 500 D) (R. Bruch MacFarlane, 1978).

According to PubChem, fulvic acids weigh 308 g/mol. In this report the value of 300 g/mol will be used.

Humins are large organic substances (~100000 D) that are rarely soluble in water and are therefore not regarded during this report.

Building blocks are degradation products of humic substances.

LMW-acids, which are anions at the neutral pH, with mainly carboxylic groups.

LMW neutrals are a collection of alcohols, aldehydes, sugars and other small neutral organic compounds without charged carboxylic groups.

Hydrophobic organic compounds are the group of compounds that are adsorbed on gel of the LC-OCD column. This can be determined by subtracting the total surface of the LC-OCD graph from the total amount of DOC measured. The reason these compounds do not get measured but remain on the column is their hydrophobic nature. (S. Huber et al, 2010) (J. Croft, 2012)

2.2.2 Functional groups

The way NOM adsorbs to resin is for a big part determined by the amount and type of reactive groups. The two most important acid groups are phenolic and carboxylic groups, which are especially present in the 'humic substances' NOM fraction.

Phenolic groups are chemical groups consisting of a hydroxyl group with an aromatic hydrocarbon group. Phenols usually deprotonate at mildly high pH values and are usually barely relevant at neutral and acidic pH. Carboxylic groups are compounds that contain carboxyl groups (R-COOH). Smaller carboxylic acids are easily soluble in water due to its polar nature, which it has by being both a hydrogen donor and acceptor. Larger molecules usually have larger alkyl chains, which mean their hydrophobic nature makes it harder to dissolve in water and the lack of charge of alkyl chains make the charge per atomic weight of the total molecule decrease.

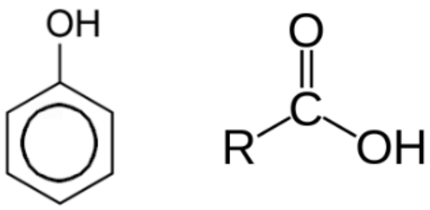


Figure 11: Phenolic and carboxylic group (schematic)

The matter in which these functional groups are active is much dependent on the pH of the water in which the NOM is dissolved. The negative charges of NOM becomes less once they drop into the acid range until it reaches the point of zero charge (PZC). The PZC is unique for each specific NOM type and is the point where the reactive groups will not be charged at all, which typically happens at a pH of around 2 to 3. (J. Ritchie and E. Perdue, 2002)

2.3 Water chemistry modeling

PHREEQC is a computer modeling program designed to perform aqueous chemical calculations. It is initially designed to solve geochemical problems but has shown to also be usable in drinking water applications (P. de Moel et al., 2012) and ion exchange (although almost exclusively with cations) in particular (C. Apello, 2002). In PHREEQC the most common water related chemical equilibriums are stored in a database and can be used to predict results of chemical processes if the starting water matrix is also known. Since PHREEQC can distinguish different phases of molecules (solid, liquid, gas) the program is able to simulate more complex process as precipitation or the carbonate equilibrium (L. Pötter, 2021) (see also attachment I). The advantage over other water chemistry programs is that it can work with a large number of chemical equilibriums that are simultaneously being calculated (P. Lu et al., 2022).

Unknown parameters

Since every NOM sample is unique, data should be collected with experimental research. In this way it can be incorporated in the PHREEQC model. In the most adsorbable organic matters a large fraction of the molecules consists of humic and fulvic acids, therefore these need to be studied in the experiments. It should be noted that those results will likely only give a general indication of chemical properties of NOM as there is such a variety in NOM types. Future research with other waters or resins needs to be done with the respective NOM isolated from that specific water type.

Information needs to be found on chemical properties of anions such as:

- Selectivity: the affinity to resin, especially compared to other anions. How likely will the NOM adsorb on the resin based on the counter-anion of that resin and the other anions present in the water matrix?
- Equilibrium constant: how do NOM and other anions such as nitrate and sulfate individually balance out with chloride on the resin? Since PHREEQC works with individual equations related to a reference ion, the K values of each target anion related to chloride is required for the model.
- Molecular size: knowing the size distribution of the NOM sample gives information on what types of fractions are in the sample. Having a lot of humic substances makes it much more likely that that more NOM will be removed with ion exchange.
- Charge of the molecules: The charge of reactive groups on NOM changes when the pH of the sample changes.The values and rate of change over pH of the charge of the NOM is different per sample as shown with titrations with various NOM samples (J. Ritchie, 2002)
- Anion exchange equivalence: This is the amount of counter anions that come off resin during adsorption with NOM. This value depends on the charge and the selectivity of NOM and the type of counter ions used.

3. Materials and methods

Jar tests and NOM titrations were performed focusing on the following aspects:

- Influence of pH on anion exchange and NOM removal
- Sulfate and nitrate spiking to determine K values for modeling purposes
- NOM spiking with several NOM samples to determine the exchange equivalent value and the K-value for modeling purposes
- Effects on NOM removal in the presence of competing anions with a high affinity (like sulfate)

3.1 Jar test procedures

Several SIX jar tests were performed (using both milli-Q and regular SIX influent, spiked with anions and/or NOM, possible pH adjustments) The description below is how such a jar test is usually performed in general.

Materials:

- Shenzhen ZR 4-6 jar tester
- pH meter
- Spectrophotometer (Hach Lange DR6000)
- Mettler PJ3600 Deltarange weighing scale
- Hach Lange test kit LCK 153 Sulfate (4-150 mg/L)
- Hach Lange test kit LCK 311 Chloride (1-1000 mg/L)
- Hach Lange test kit LCK 339 Nitrate (0.23-13.5 mg/L)
- Petri dishes
- Beakers
- Jerry cans
- Pipette
- Pipette tips
- Syringe
- 5 cm cuvette
- 1 cm and 5 cm cuvette
- Whatman Spartan 30/0.45 RC Filter Units

Method:

The water samples taken from the SIX pilot plant were stored in a jerry can in advance to adjust to room temperature (around 20 °C). The sample was then spiked or had its pH adjusted while in the jerry can to make sure these jars will contain the exact same water when dividing the sample over the six 1.5 L jars in the jar tester. This minimizes errors in manually spiking each jar. The jars were stirred sufficiently (200 RPM) to make sure the sample is a homogeneous solution, the resin could get in contact with the target anions and the resin would not settle. The baffles in the jars are to prevent a vortex in the jar to form. At this point additional adjustments, as spiking or pH correction, to each jar was made, if necessary. For each jar, the pH, UVT and relevant anion concentrations were determined.

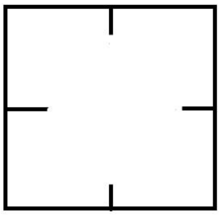


Figure 12: Schematic topview of jar with baffles

The resins were added in the required concentrations, ranging from 1 g/L to 30 g/L, simulating dosing rates in the full scale process. The jars were stirred for around 30 to 60 minutes to assure equilibrium is approached. Figures 14 and 15 below show how this short reaction time is sufficient as a jar test will approach equilibrium state closely for fresh resin and for several months old resin sampled from the full scale SIX treatment plant (the PSA) and the SIX pilot plant, considering the original UVT of lake Ijssel water is approximately 81%. It was possible to retrieve smaller samples from the jars during the jar test at desired time stamps using the taps in the jars to analyze the process over time. The final sample and the smaller samples were tested on their pH, UVT and anion concentrations.

Figure 13: Shenzhen ZR4-6 jar tester

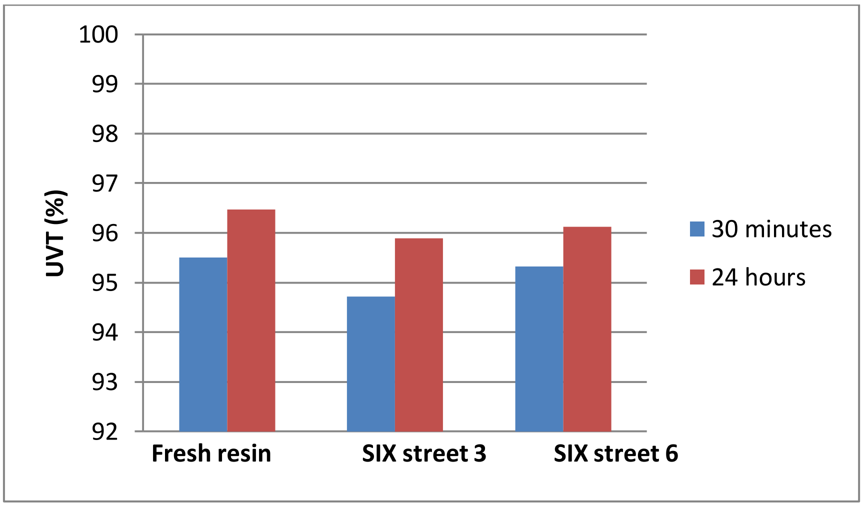


Figure 14: UVT values of SIX influent, treated with fresh resin and multiple times regenerated SIX resin from the treatment plant, after 30 minutes and 24 hrs of jar test treatment

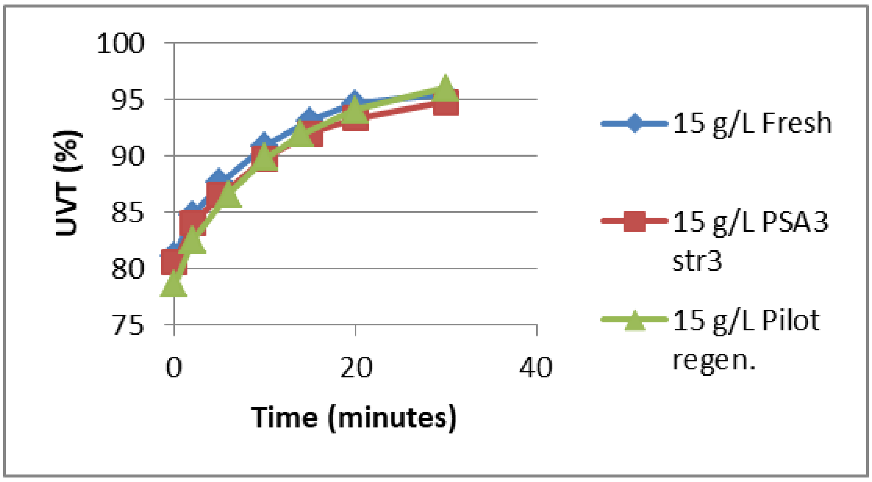


Figure 15: UVT improvement of Lake Ijssel water during IEX jar test with 15 g/L resin (fresh resin, resin from the full scale treatment plant and the pilot plant)

In figure 18 a comparison is made between fresh resin and resin that has been been regenerated multiple times to show that multiple cycles of regeneration have no effect on UVT increasing abilities of the resin.

Several Hach Lange test kits are used to measure most of the ion concentrations on site. Samples are sent to Het Water Lab in Haarlem for analyzation to measure DOC and bicarbonate. The UVT is determined by reading the adsorbance at 254 nm of a cuvette with sample water. UVT can be used as a surrogate parameter for DOC because they have a quasi-linear relation in one water sample as shown in the figure below.

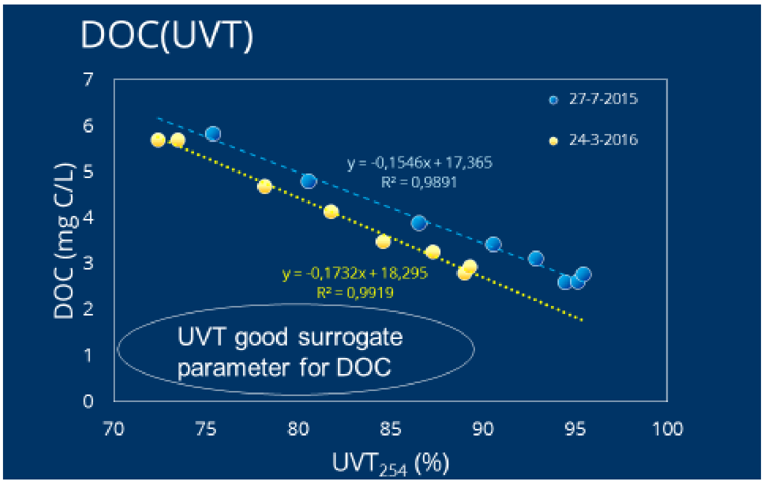


Figure 16: Linear relation between UVT and DOC for Lake Ijssel water, E. Koreman (2016), *NOM removal by Suspended Ion Exchange (SIX)* (PowerPoint presentation of DOC2C workshop 3-9-2016)

After calibrating the spectrophotometer with a demi water blanc the samples are filtered through Whatman Spartan 30/0.45 RC Filter Units into the cuvette with the help of a syringe. These Filter Units have to be flushed with demi water before used since the dry filters may contain some initial DOC which could influence the results.

The absorbance and transmission values are related in a logarithmic way. After measuring the ultrviolet absorbance (UVA) in a spectrophotometer with a cuvette of length x cm, the transmission can be calculated via:

$$\text{UVT} = 10^{\frac{UVA}{x}} * 100\% \qquad (5)$$

Figure 17: Hach Lange DR6000 spectrophotometer

Jar tests

The following jar tests were performed with SIX influent, obtained from the SIX pilot plant at Andijk III. These samples are treated with different pH adjustments and resin concentrations to observe basic kinetics within the ion exchange treatment of raw water. SIX influent is softened lake Ijssel water and has a pH of 8 by default.
Bench scale tests were performed as well, using a 60 L vessel instead of the standard 1.5 L jars to determine the consistency of the jar test results on different scales and to be able to draw larger samples for determination of bicarbonate and DOC.

- SIX influent with various resin concentrations
- SIX influent with higher pH with various resin concentrations
- SIX influent with lower pH with various resin concentrations
- Bench scale SIX influent with higher and lower pH

To determine the K value of different anions and observe the effects of competition between different ions and the differences with a higher pH the following jar tests were performed. The relevant anions have been dissolved in purified water and given sufficient time (at least 1 hour) to dissolve and diffuse.

- Milli Q with nitrate (50-100 mg/L)
- Milli Q with sulfate (100-250 mg/L)
- Milli Q with sulfate (236 mg/L) with low resin concentrations (1-6 g/L)
- Milli Q with nitrate and sulfate (similar to above, ranging from nitrate dominance to sulfate dominance to study anion competition)
- Milli Q with nitrate and sulfate at higher pH (pH ~8 instead of ~4)

The following jar tests were done with NOM samples dissolved in purified water in different concentrations to determine their counter anion equivalence. By measuring the amount of chloride increase in the water and the amount of DOC (the carbon fraction of DOC) removed it can be determined how many chloride ions exchange per weight of DOC. If the molecular weight of the DOC is known (or estimated) the chloride equivalence per molecule DOC can be calculated. The increased pH was to study the charge and the anion equivalence of NOM under different pH circumstances. The experiment with sulfate is to observe the effects of competition of a high selective anion on the NOM removal.

The following NOM samples were available to be used in the experiments:

- Jadis Additiva Fulvic Clean®
- PWN Fulvic acids (brine from IEX regeneration loaded with Lake Ijssel water, the Netherlands)
- PWN Humic acids (brine from IEX regeneration loaded with Lake Ijssel water, the Netherlands)
- Water groep Fulvic acids (brine from IEX regeneration loaded with surface water from Den Blankaert, Belgium)

The Fulvic Clean sample is a NOM based supplement produced by Jadis Additiva.(Jadis additiva website) It is a combination of fulvic and humic acids that can be consumed by humans and animals to help with health of intestines. The other samples are NOM samples that are obtained by isolating it from IEX brine.

These samples are all obtained through the NOM isolation method developed by the International Humic Substances Society (IHSS). This is done by adsorption of NOM in the brine with XAD-8 resin combined with alkaline extraction to eluate the hydrophobic fraction with NaOH and freeze-drying to extract the NOM from the water into a powder sample. The humic and fulvic acids can be separated by bringing the pH towards 1, where humic acids precipitate due to not being able to dissolve under those conditions, while fulvic acids will remain dissolved under these conditions

- Milli Q with NOM
- Milli Q with NOM at higher pH
- Milli Q with PWN fulvics and sulfate
- Milli Q with PWN humics and sulfate

3.2 Titration procedures

Using the results of the jar tests with NOM samples the exchange equivalence values for each NOM type were determined. This gives valuable information about the relation between the amount of DOC and the amount of chloride they exchange with. It has been noted that this relation is different for each NOM type, which suggests that different molecules and molecule groups within the DOC contribute for different amount of chloride exchange.

It is however unclear what types of molecular groups are responsible for the actual exchange. For this reasons a set of titrations is done to determine the charge of the NOM for different pH values. The different types of molecule groups that make up the DOC are more active at certain pH values. Their charge will change with the pH and have more buffering capacities to take up titrant ions. At first it is mainly the weak acid groups that react, such as carboxyl groups. Only when most of these groups are exchanged with resin, other functional groups such as phenol groups will start reacting, (although in practice it rarely comes to this situation as this happens around pH 9 which is an unusual value in drinking water production). With this information the performance of resin on to be studied type of NOM can be predicted more accurately with the help of a relatively simple and less time consuming titration test.

To make sure the entire pH range where NOM has charge was taken into account, the titration has to start at or before the point of zero charge (PZC). NOM has a PZC from around 2.7 to 5 (J. Ritchie, E. Perdue (2002). The PZC of the available samples are unknown, so to make sure the titration starts below PZC, the NOM samples are acidified to below 2.7.

Materials:

- NOM samples
    - PWN fulvics
    - PWN humics
    - Watergroep fulvics
    - Jadis Additiva fulvics
- Metrohm 702 SM Titrino titrator
- Magnetic stirrer
- 0.1 M NaOH solution
- Sodium chloride
- Beaker glasses

Method:
Around 15 mg of NOM sample is dissolved in 50 mL (to get 300 mg/L) 0.1 M NaCl solution, which functions as a background electrolyte. A magnetic stirrer keeps this sample in a homogeneous solution. The jar contains an airtight lid and is stirred not too excessively to make sure the atmosphere has minimal influence on the carbonate equilibrium and pH of the sample. Enough 0.1 M HCl is added (typically 1 or 2 mL) to make sure the pH at the start of the titration is below 2.7 (lowest point of zero charge found for NOM in literature). Then 0.1 M NaOH is dosed in steps of 0.006 mL until the pH reaches at least 10.5 using the titrator, which had been calibrated at each day of operation. At every step the pH is measured and stored. Each titration lasted for 30-45 minutes.

Data processing

The relation of titrant volume and pH can be translated into organic charge density Q (meq/gC). This is the organic charge of the NOM in the solution devided by its carbon contents.

$Q = 1000*(Sum[Org^-]/DOC)$ (6)

To determine the organic charge the blanc titration curve is subtracted from the NOM titration curve to obtain the NaOH that is used to deprotonate the carboxylic acid groups on the NOM. Below an example this is presented where the arrow shows how the difference between the two titrations represents the NaOH reacting with the NOM:

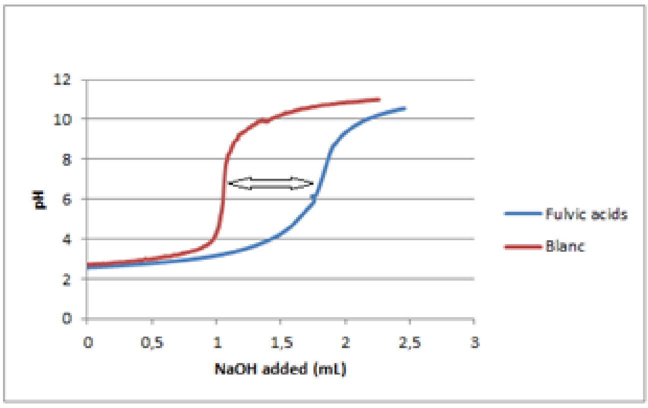


Figure 18: Fulvic acid and blanc titration curves, with the NaOH fraction reacting with the NOM displayed with the arrow

Alternatively the organic charge can be determined by setting up the charge equilibrium for every titration step. Since the concentrations of all other ions are known for every titration step, the organic charge can be calculated for every step. Unfortunately this can give extreme values at high and low pH (J. Ritchie, 2002) and therefore only the subtraction method will be used. A more thorough explanation of this method with charge equilibrium can be found in attachment G.

4. Results

The results of the jar tests, the titrations and the modeling are displayed in this chapter.

4.1 Jar tests with SIX influent

These results are from the jar tests and bench scale tests performed with SIX influent (softened lake Ijssel water) that has gotten in contact with 15 g/L resin, the regular dosing in the full scale SIX process. The only changing variable between each individual experiment is the pH which was increased or decreased with either NaOH or HCl respectively.

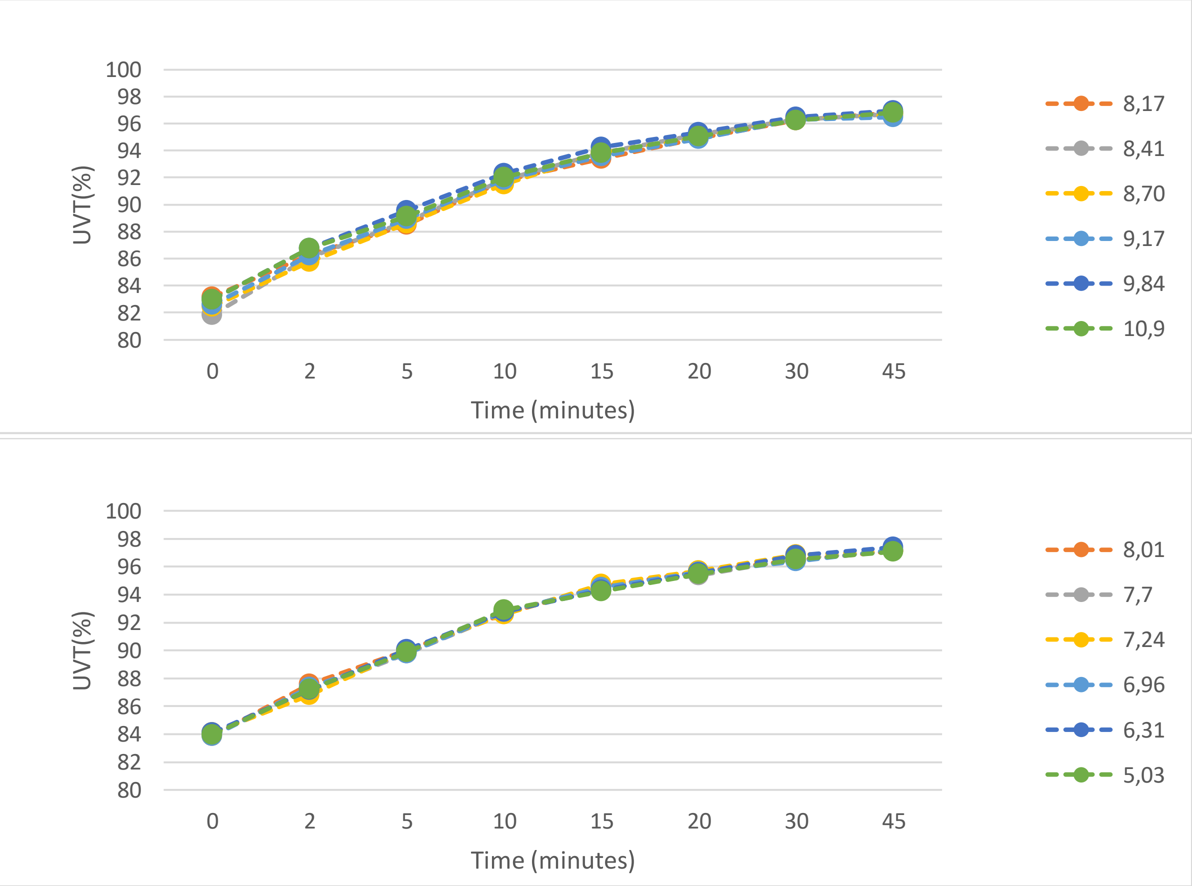


Figure 19: UVT values for jar tests with alkaline (top) and acidic (bottom) pH values

In figure 19 the UVT values during a jar test of SIX effluent and resin are shown. Due to the overlapping curves it is clear that increasing the pH has no effect on the removability of natural organic matter on a wide range between pH values of 5.03 and 10.9.

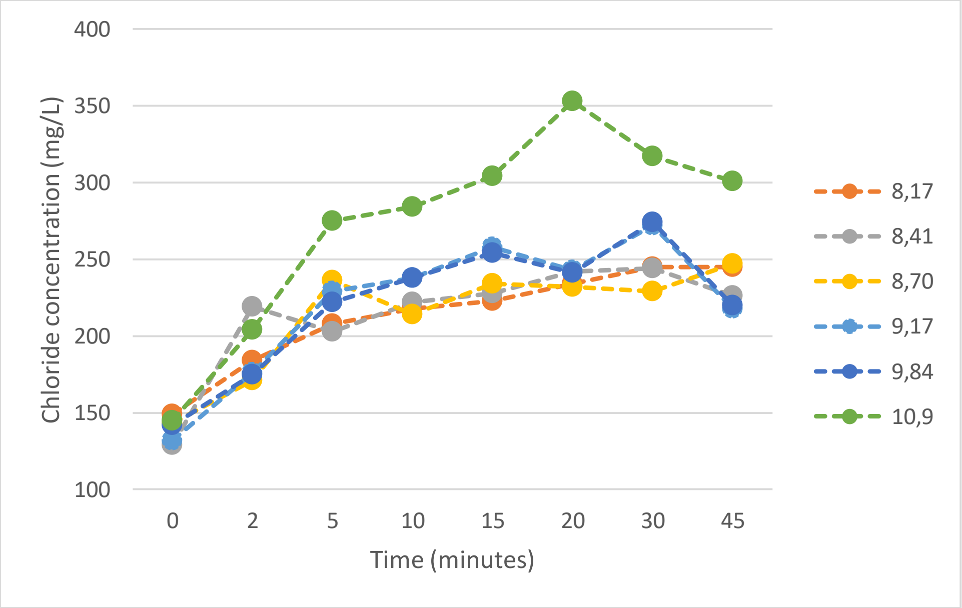


Figure 20: Chloride values for jar tests with alkaline pH values

Figure 20 shows the chloride concentrations during the same experiment. It is notable that while the UVT stays the same, the chloride release of the resin increases for pH=10.9 values. This is most likely due to the increased amounts of (bi)carbonate dissolving from the air into the water during the experiment, adsorbing on the resin and therefore releasing more chloride from the resin. Also there is probably more carbonate in the water at this pH and less bicarbonate. The exchange of a multivalent ion will release more chloride ions form the resin compared to a monovalent ion.

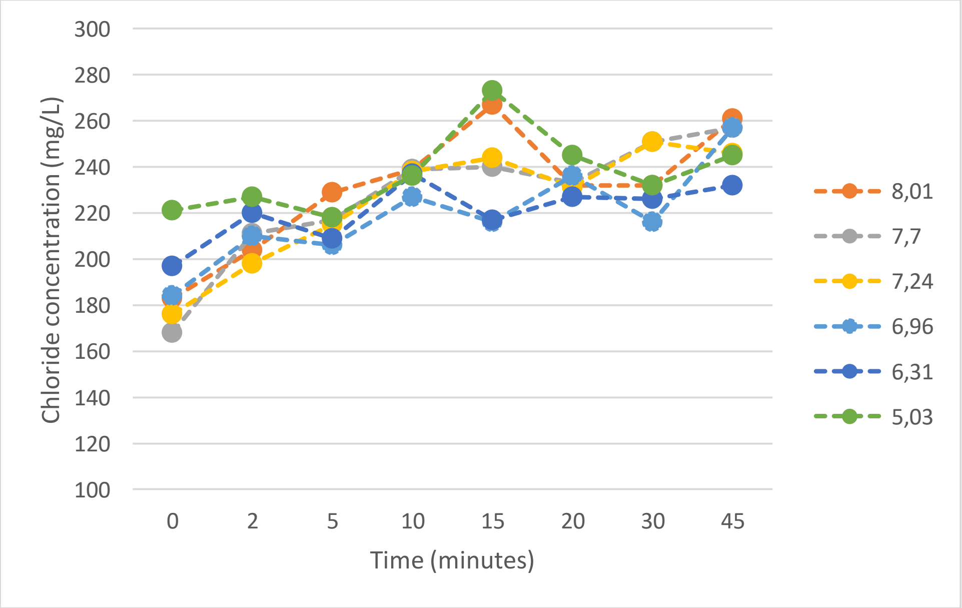


Figure 21: Chloride values for jar tests with acidic pH values

Figure 21 shows the chloride values for the same experiment as figure 24. It should be noted is that the chloride concentration at the start of each experiment is different due to the addition of the HCl used for acidification. The figures show how water with higher pH will cause the exchange resin to release more chloride, especially beyond pH 10 where big shifts in the carbonate equilibrium start to happen increasing the bicarbonate concentrations. Since UVT's are unchanged suggesting that removal of natural organic matter is unchanged by pH changes, this means that the differences in chloride release are caused by the presence and adsorption of bicarbonate.

Bench scale tests

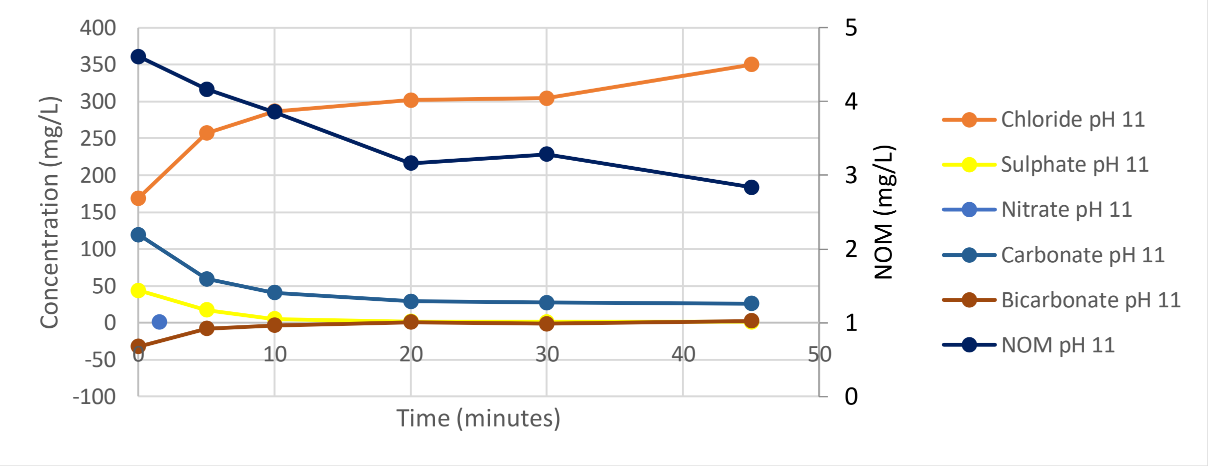


Figure 22: Anion concentrations during bench scale test with SIX water and pH 11

Figure 22 shows the anion concentrations during the bench scale test with pH 11. It is notable that at this pH the carbonate levels get so high that they are by far the most present adsorbing anion in the system. This explains why the chloride concentrations in figure 20 are higher at pH 11 (carbonate is multivalent). Despite this, the sulfate is almost entirely adsorbed within 10 minutes despite having a starting concentration that is only half of that of carbonate. This shows that selectivity is important in the removal of anions.

Also it is clear that DOC adsorption is only small compared to the total adsorption of anions. This shows that competition of other anions can have a major influence on the DOC sorption, especially if those anions have a high selectivity such as sulfate.

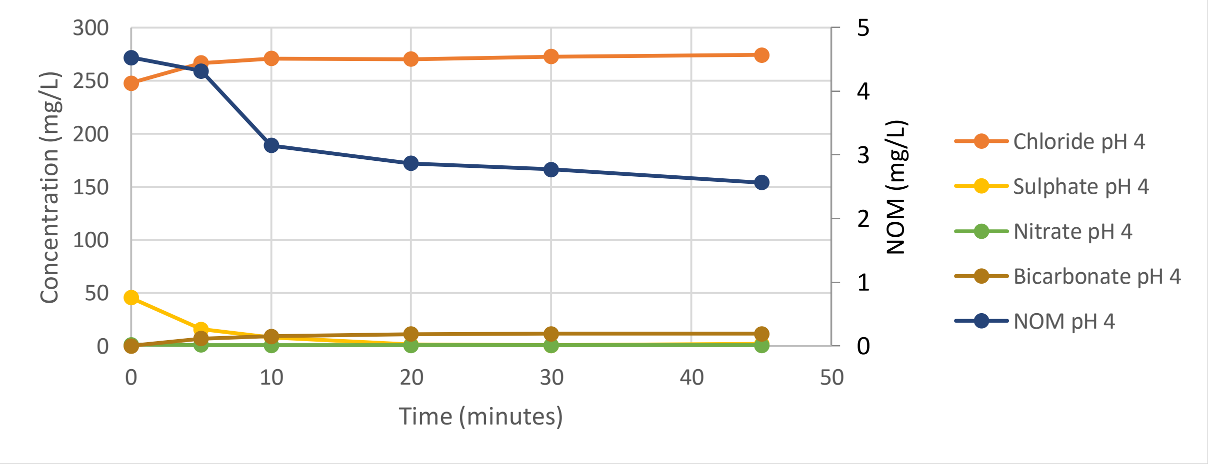


Figure 23: Anion concentrations during bench scale test with SIX water and pH 4

In figure 23 the bench scale results for low pH are shown. In this situation, the sulfate is the anion with the highest affinity, due to the lack of carbonate. One observation is that the bicarbonate increases over time. This is most likely due to the low pH water sample getting in contact with the atmosphere, allowing carbon stripping to happen, this is increasing the pH and CO_2 is transferred into bicarbonate because the carbon equilibrium is shifting.

In figures 22 and 23 it is visible how the chloride increases over time but approaches equilibrium towards the end. This shows that the ion exchange resin under these circumstances indeed needs around 30 minutes reaction time to adsorb almost all target anions. These final chloride values vary 30 mg/L (around 300 mg/L for pH 11 and around 270 mg/L for pH 4.6). This equals to 30/35.45 = 0.85 mmol/L of chloride.

The carbonate level in figure 22 gets reduced from 120 to around 25, which means that around 95 mg/L of carbonate was removed. 95/60.01 (g/mol) = 1.58 mmol/L. Due to the divalent charge of carbonate the adsorption would release around 1.58/2 = 0.79 mmol of chloride. This shows that the difference in chloride levels between figures 28 and 29 is practically entirely caused by the adsorption of carbonate, and therefore sulfate and (bi)carbonate are in the most relevant anions in regards of controlling the chloride increase during SIX for lake Ijssel water.

4.2 Jar tests with isolated anions

The full results of these jar tests can be found in attachment C.

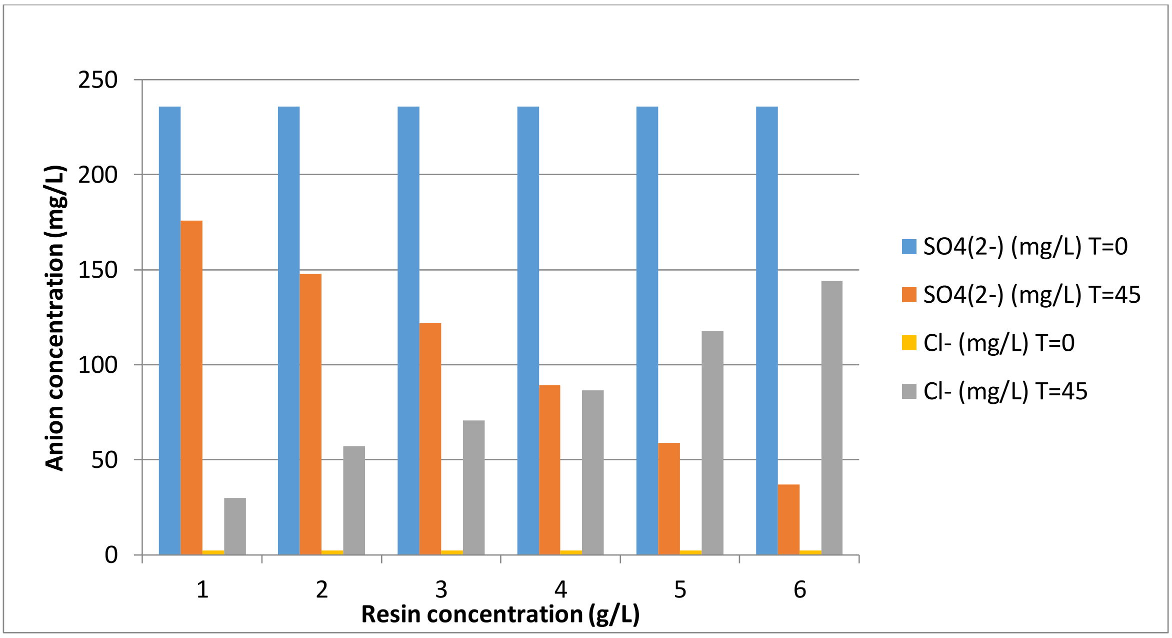


Figure 24: Sulfate and chloride concentrations before and after jar tests with low resin concentrations (constant sulfate concentration of 236 mg/L, resin concentration ranging from 1-6 g/L)

As can be observed in figure 24 above, using low resin concentrations is required to obtain a sulfate concentration in the effluent that is big enough to do equilibrium calculations with.

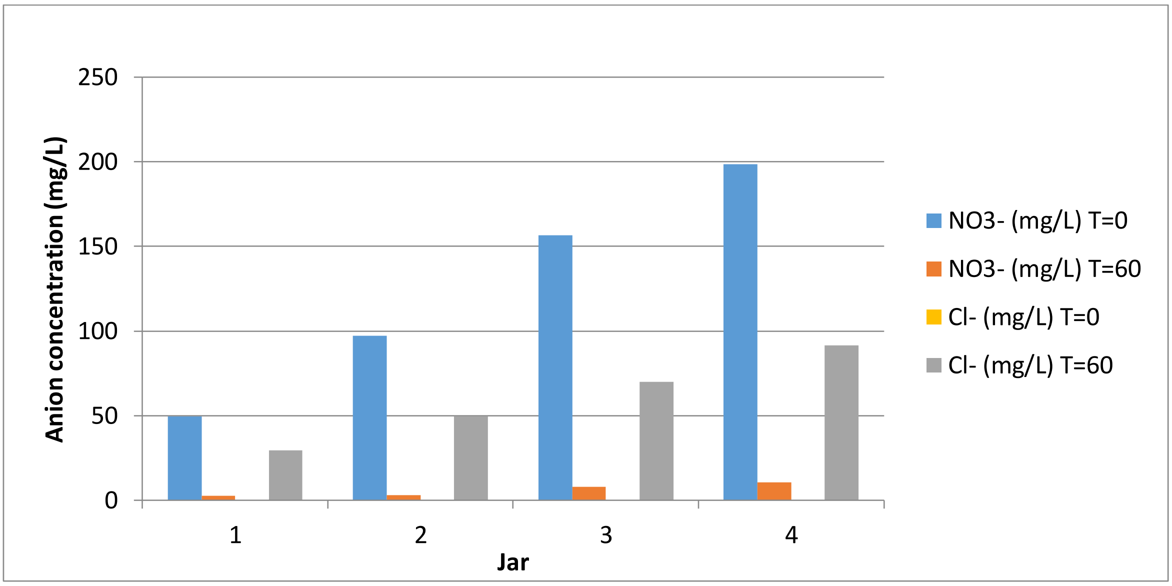


Figure 25: Nitrate and chloride concentrations before and after jar tests (20 g resin/L in all jars) Nitrate concentrations ranging from 50 mg/L to 200 mg/L

The nitrate concentrations in the effluent are high enough so that the K value of nitrate can be determined.

To test the effects of competition and pH on adsorption of isolated anions, experiments with a combination of sulfate and nitrate were performed. In these experiments the sulfate and nitrate concentrations were mixed in various combinations ranging from sulfate dominating to nitrate dominating.. The first series was done at pH 6 while the second series is done at a pH of 8.8 to study effects of pH.

4.3 Jar tests with NOM samples

To be able to study natural organic matter concentrations before and after ion exchange, DOC percentages of the NOM samples are required, as only TOC/DOC was measured. For each NOM sample the DOC concentration was measured to be later converted back to DOC/NOM ratios. The results are displayed in the table below:

Table 2: Average DOC/NOM relations for Jadis additiva fulvics, PWN fulvics and humics and Watergroep fulvics

NOM sample	DOC/NOM relation
Jadis additive fulvic acids	32 %
PWN fulvic acids	47 %
PWN humic acids	44%
Watergroep fulvic acids	46 %

Figures 26 and 27 below show the relation between adsorbed NOM and released chloride ions after ion exchange with S5128 resin.

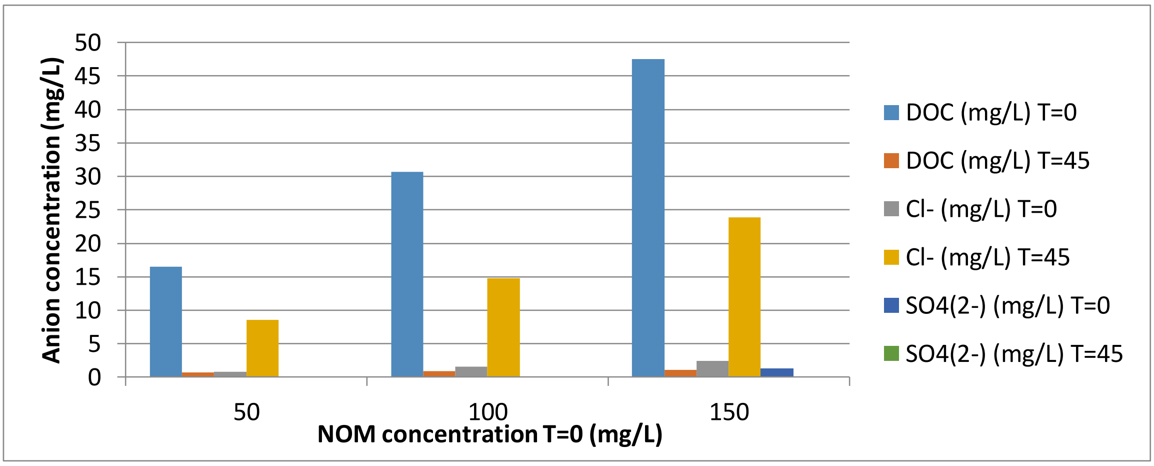


Figure 26: Jadis additiva fulvics jar tests, pH=7.2 (15 g resin/L)

Jadis additiva fulvic acids shows excellent removal capacity. Around 0.13 mg of Cl^- is released per mg NOM.

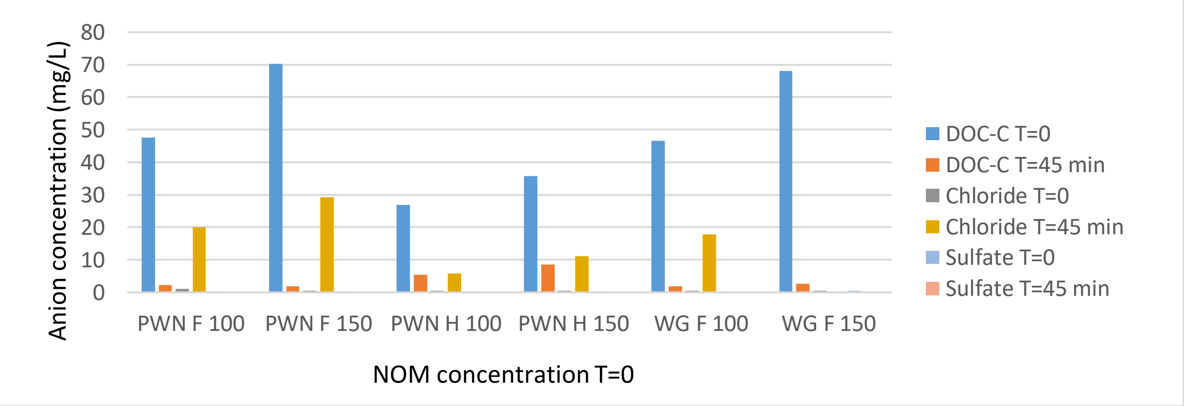


Figure 27: PWN fulvics (PWN F), humics (PWN H) and Watergroep fulvics (WG F) jar tests, starting concentrations 100 and 150 mgNOM/L for each sample respectively, pH=7.8 (15 g resin/L)

Figure 39 above shows the adsorption of PWN fulvic acids, humic acids and Watergroep fulvic acids at concentrations of 100 mg/L and 150 mg/L respectively. It's notable that all organic carbon gets adsorbed by the resin and that the chloride release from the resin is constant.

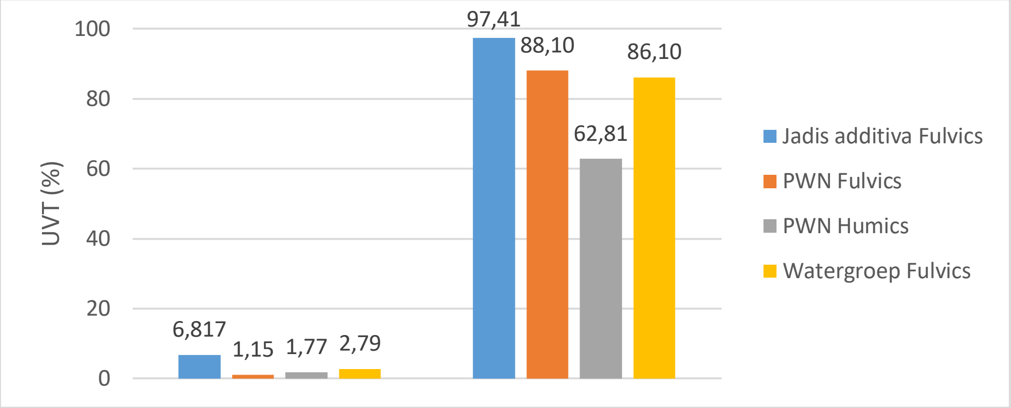


Figure 28: UVT values of NOM samples (100mg/L) before and after SIX jar tests (15 g resin/L)

Figure 28 shows clearly that UVT is extremely low initially and increases tremendously after IEX treatment, indicating that also with these samples containing natural organic matter UVT can be used as an indicator of DOC concentration.

The majority of all samples are removed through jar tests, which is expected since the samples originate from brines consisting of NOM that is released from an ion exchange resin during regeneration.

Unfortunately the NOM concentrations in the effluent during the jar tests is quite low to calculate reliable equilibrium constants for use in PHREEQC. Therefore another series of jar tests with PWN fulvics and humics are performed with low resin concentrations. The results are presented below. The pH was between 7.5 and 8 to ensure enough charge in the NOM and give the results practical use as this neutral pH is common in surface water entering water treatment plants. Also, sulfate has been added to study the adsorption of NOM while there is a competing compound in the feed water.

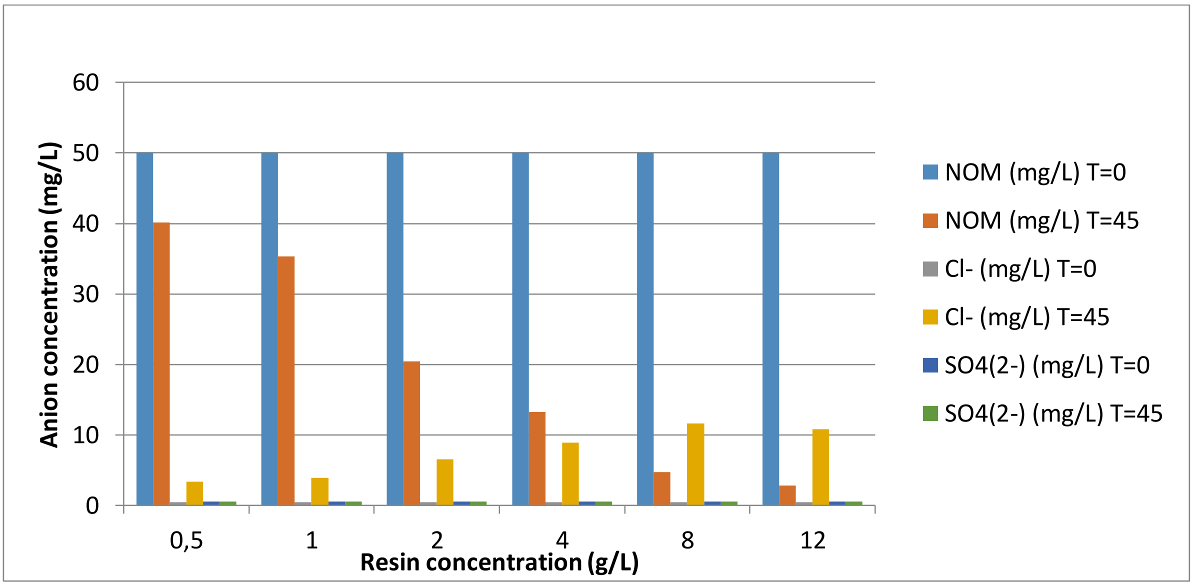


Figure 29: PWN fulvics jar tests at low resin concentrations, pH=8 (0.5-12 g resin/L)

Figure 29 clearly shows a trend of increasing NOM adsorption when the resin concentration increases. This indicates that at resin capacity takes up a bigger role here than the selectivity of NOM.

Table 3: Chloride exchange equivalence values for PWN fulvic acids

Resin conc (g/L)	0,5	1	2	4	8	12
dCl/dNOM (mol/mol)	2,52	2,02	1,76	1,94	2,09	1,86

Table 3 above shows the counter anion exchange equivalence values of PWN fulvic acids. Around 2 mol chloride gets released per adsorbed mole of NOM. This suggests that PWN fulvics has similar selectivity as sulfate.

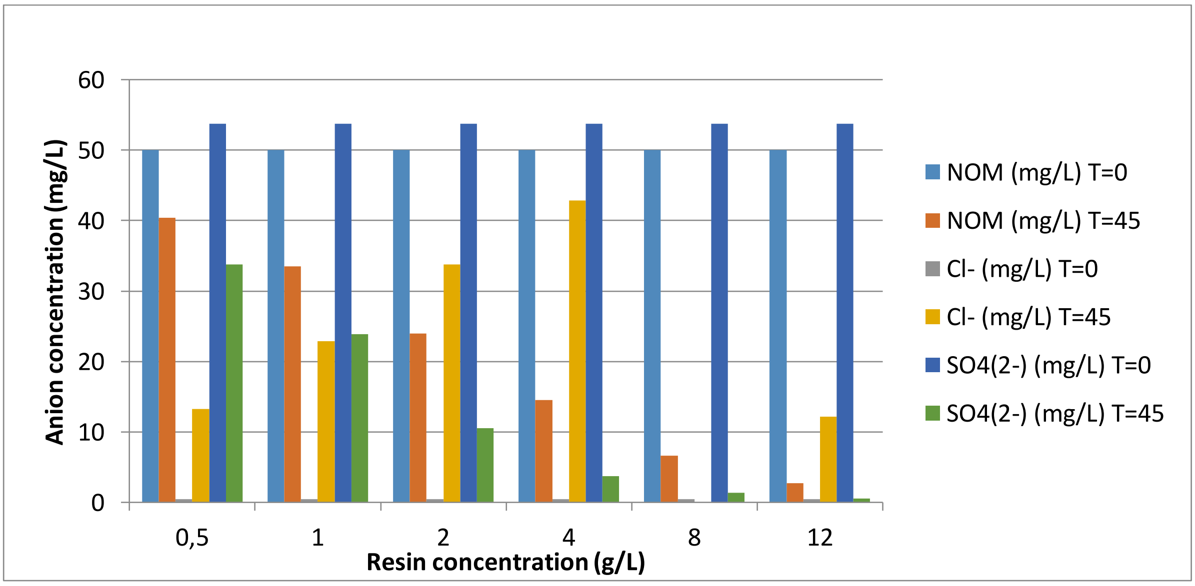


Figure 30: PWN fulvics and sulfate jar tests at low resin concentrations, pH=8 (0.5-12 g resin/L)

When sulfate is added as well, the NOM adsorption is barely affected, even though the majority or even all sulfate gets adsorbed. This is remarkable as table 2 showed that both of these target anions are in the same order of magnitude of selectivity. It should be noted that for resin concentration 8 g/L the chloride in the effluent is not taken into account as it was exceptionally high probably due to a measuring error.

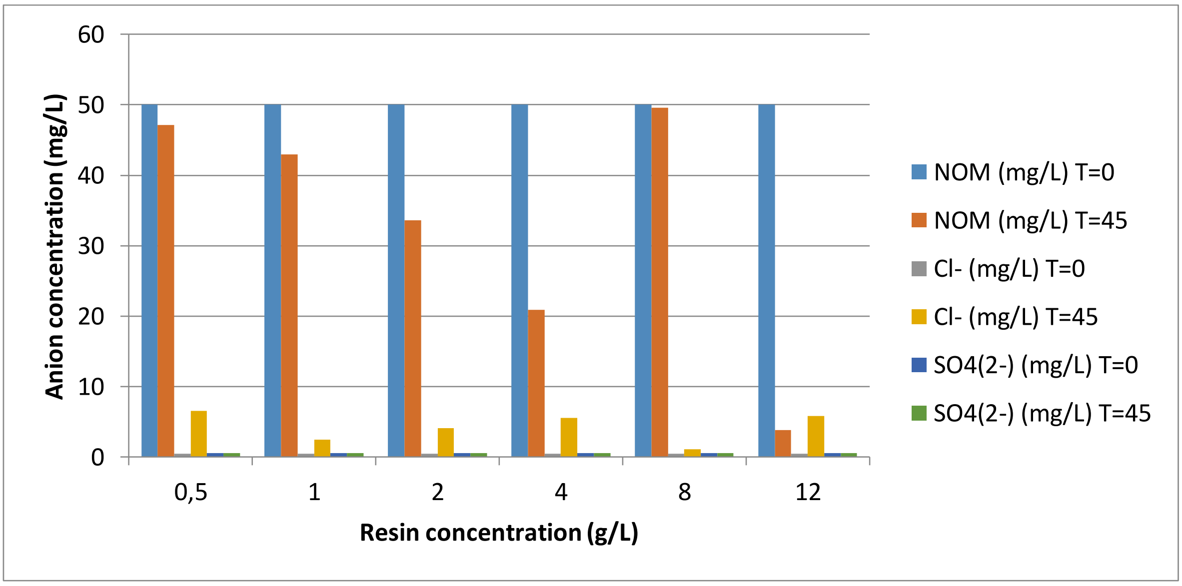


Figure 31: PWN humics jar tests at low resin concentrations, pH=8 (0.5-12 g resin/L)

For resin concentration of 8 g/L the NOM concentration seems to have an error at T=45 minutes. Despite this the trend for humic acids adsorption is quite clear and similar as with fulvic acids.

Table 4: Chloride exchange equivalence values for PWN humic acids

Resin conc (g/L)	0,5	1	2	4	8	12
dCl/dNOM (mol/mol)	60,47	8,14	6,30	5,01	41,91	3,27

Table 4 shows an anion exchange equivalence that is even higher than with the fulvic acids. Around 3 to 8 mol chloride gets released per mol NOM. This means that an average humic acid molecule has 3 to 8 reactive groups.

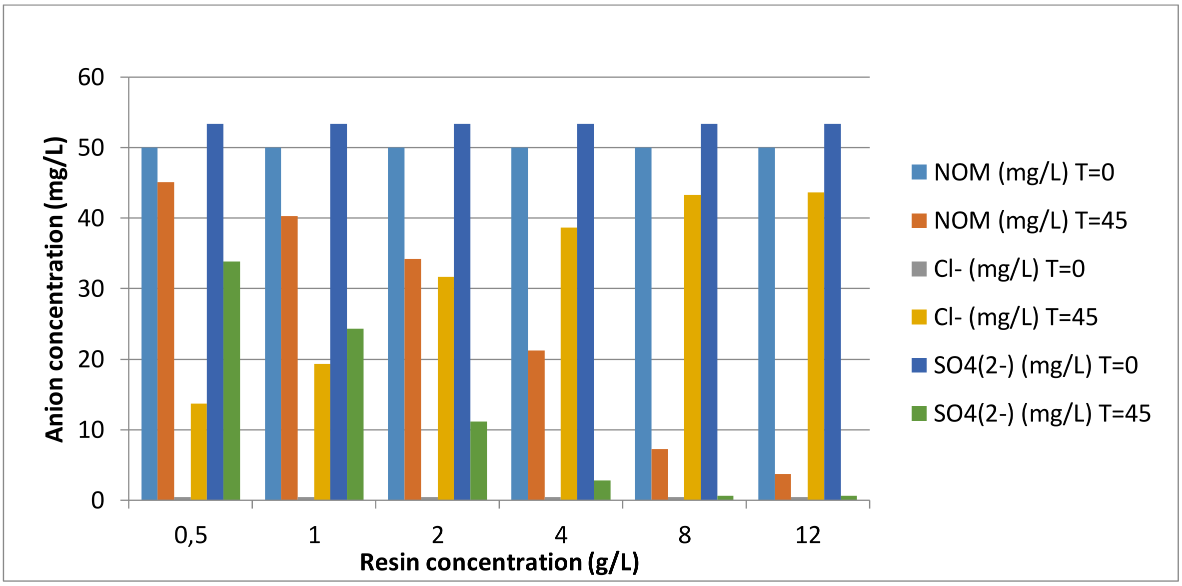


Figure 32: PWN humics and sulfate jar tests at low resin concentrations, pH=8 (0.5-12 g resin/L)

In the case of both humic acids and sulfate, the humic acids adsorption does not suffer from the competition just like fulvic acids. For low resin concentrations sulfate gets adsorbed in larger percentages than humic acids indicating that the selectivity of humic acids comes close to that of sulfate but should not be higher.

4.4 Titrations

The titrations resulted in several NaOH-pH curves. The blancs (figure 18) were subtraced from these curves and then the dosed NaOH was converted into charges for each sample using the organic charge (equation 6). Below the results curves are presented as titration curves. The point of zero charge of NOM is set at Q=0.

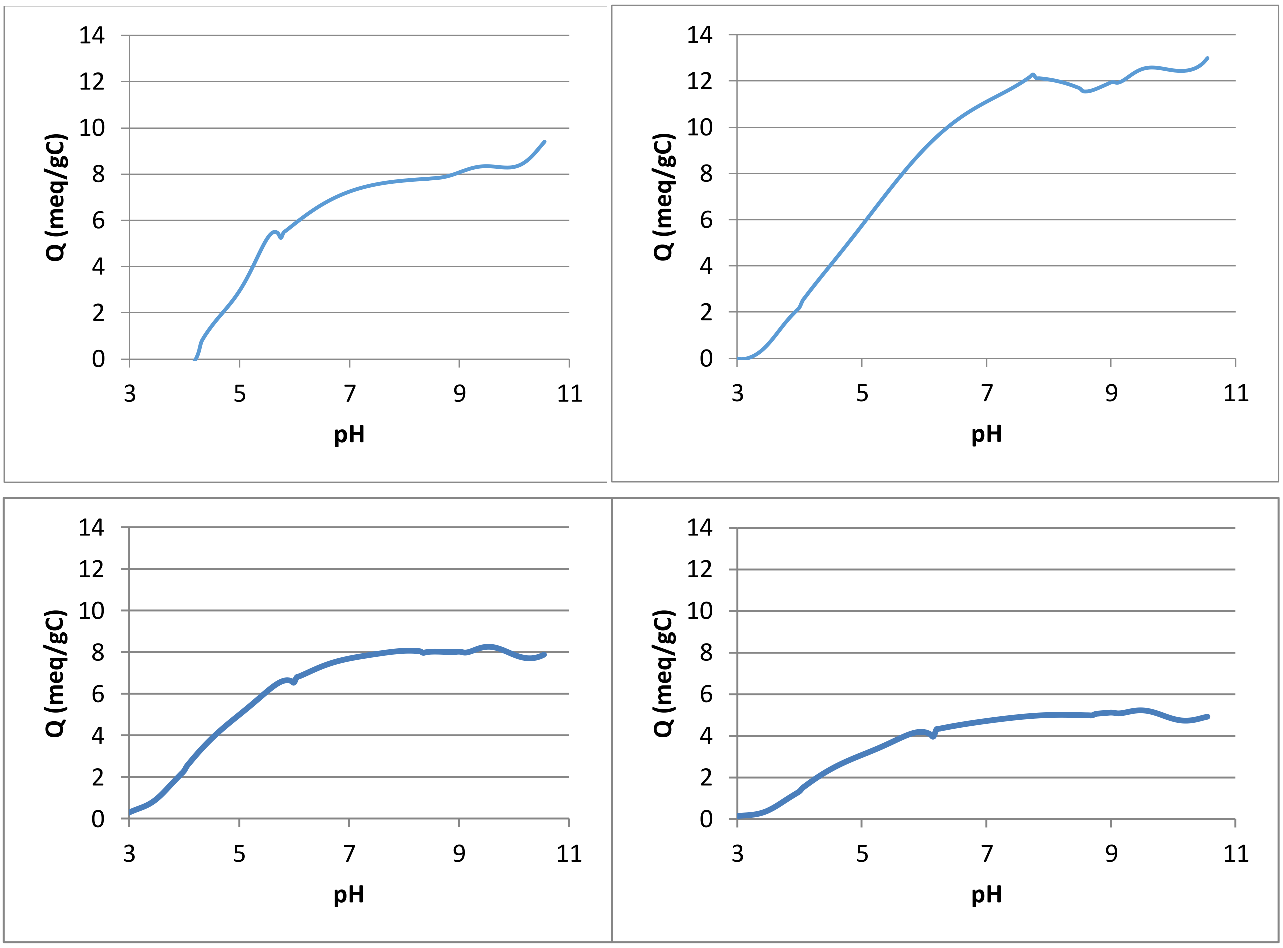


Figure 33: Charge density from titration experiment with Jadis additiva fulvic acids (top left), PWN humic acids (top right), PWN fulvic acids (bottom left) and Watergroep fulvic acids (bottom right)

The two most common molecular groups in natural organic matter, carboxyl groups and phenolic groups, can be derived from these graphs due to the relation between the charge increase over the pH range. According to Perdue (2014) carboxylic groups contribute to the NaOH take up until the pH reaches 8. Then two times the amount of NaOH used between pH 8 and 10 is an indication of the amount of phenolic acids:

Table 5: Estimations of the carboxylic and phenolic activity in the NOM samples

NOM sample	Carboxylic charge (Org^-/DOC)	Phenolic charge (Org^-/DOC)
Jadis additiva fulvics	7,9	1,2
PWN humics	12,07	0,8
PWN fulvics	8,05	0
Watergroep fulvics	5	0

4.5 PHREEQC results

By determining the equilibrium constants for the various anions and NOM samples in regard of ion exchange with chloride on Lewatit S5128 resin, the reactions can be modeled in PHREEQC. Furthermore PHREEQC needs concentrations of ions and pH of the influent and an exchange capacity of the resin to predict the ion concentrations left in the effluent. These values are then compared with experimentally obtained numbers in graphs.

4.5.1 Equilibrium constants

Nitrate

Using the data from figure 32, we can determine the K value as the concentrations of chloride and nitrate on the resin and in the water are known.

$ClZ + NO_3^- <> NO_3Z + Cl^-$

Using the β as the fraction of target anion on the resin compared to the total amount of exchange spots on the resin (Apello and Postma) we then get the following K value:

$$K = \frac{\beta_{NO3^-} * [Cl^-]}{[NO3^-] * \beta_{Cl}}$$

Table 6: Determination of equilibrium constant K for nitrate

Resin dosage (g/L)	20	20	20	20	Average
NO3- (mg/L) T=0	49,5	97,2	156,5	198,4	
NO3- (mg/L) T=45	2,76	2,99	7,88	10,7	
βNO3	0,030	0,061	0,096	0,121	
Cl- (mg/L)	29,5	49,6	70	91,6	
Cl- (mol/L)	0,001	0,001	0,002	0,003	
βCl	0,970	0,939	0,904	0,879	
K	0,58	1,88	1,65	2,06	1,54
log K	-0,236	0,274	0,217	0,314	0,142

Sulfate

Since we know each gram of resin contains 1.25 meq worth of sorption sites and now how much sulfate has been adsorbed, we can calculate the β_{SO4} by dividing the sulfate meq by the total amount of sorption spots (1.25 meq x resin concentration in g/L). See equation below:

$$\beta_{SO4} = \frac{(236 - [SO4^{2-}]) * 2/96.06}{1.25 * resin\ concentration}$$

where $[SO4^{2-}]$ is the sulfate concentration left in the water after adsorption in mg/L and the resin concentration is in g/L.

Using the previously presented data in table 1 this will result in the following results for β and K.

Table 7: Determination of equilibrium constant K for sulfate

Resin dosage (g/L)	1	2	3	4	5	6	
SO4(2-) (mg/L)	176	148	122	89,3	58,8	37	
βSO4	0,999	0,733	0,633	0,611	0,590	0,552	
Cl- (mg/L)	30	57,1	70,5	86,5	118	144	
βCl	0,001	0,267	0,367	0,389	0,410	0,448	
							Average
K	0,625	0,005	0,005	0,010	0,026	0,053	0,12
log K	-0,204	-2,335	-2,270	-1,998	-1,584	-1,277	-1,61

The average of these results gives a 'log K' of -1.61 which will be used in modeling sulfate adsorption on resin in PHREEQC.

NOM: fulvic acids

The same way as with sulfate, the exchanged fraction β and equilibrium coefficient K can be determined for the two NOM samples. According to A. Chabaan et al. (2016) fulvic acids typically contain 1 functional group (carboxylic) per molecule, suggesting that NOM is monovalent and exchanges 1 NOM molecule per chloride molecule :

$ClZ + NOM^- <> NOMZ + Cl^-$

This would then result in the following formulate for the equilibrium constant K:

$$K = \frac{\beta_{NOM} * [Cl^-]}{[NOM^-] * \beta_{Cl}}$$

Using the previously presented data in table 2 this will result in the following results for β and K for fulvic acids:

Table 8: Determination of equilibrium constant K for fulvic acids

Resin dosage (g/L)	0,5	1	2	4	8	12	Average
NOM (mg/L)	40,18	35,34	20,43	13,31	4,73	2,85	
βNOM	0,003	0,003	0,003	0,002	0,001	0,001	
Cl- (mg/L)	3,387	3,954	6,6	8,877	11,634	10,806	
βCl	0,997	0,997	0,997	0,998	0,999	0,999	
K	3,94E-02	3,85E-02	1,12E-01	1,42E-01	3,19E-01	3,40E-01	1,65E-01
log K	-1,404	-1,414	-0,950	-0,849	-0,496	-0,469	-0,93

However, it can be checked what the exchange equivalence is of the NOM samples used in the experiments. From the jar tests with isolated NOM and a resin concentration of 20 g/L (figures 36-39) the moles of NOM and chloride exchanged can be used to determine this number.

Table 9: Exchange equivalences for fulvic and humic acids with chloride

	PWN Fulvics		**PWN Humics**	
NOM (mg/L) T=0	100	150	100	150
NOM (mg/L) T=45	4,60	3,96	19,94	35,61
Cl- (mg/L) T=0	0,944	0,508	0,519	0,381
Cl- (mg/L) T=45	19,98	29,27	5,77	11,04
dNOM/dCl (mol/mol)	1,69	1,67	1,85	2,63

For both humic and fulvic acids the exchange equivalence is around 2. It is worth noting that the wateq database inPHREEQC also considers fulvate and humate as divalent molecules. This would suggest the equilibrium constant K is actually built up quite similar as sulfate. If this value is assumed the following equations will be obtained instead:

$2ClZ + NOM^{2-}$ <> $NOM2Z + 2Cl^{-}$

$$K = \frac{\beta_{NOM}*[Cl^{-}]^2}{[NOM^{2-}]*\beta_{Cl}}$$

This will then result in the following K values:

Table 10: K values of fulvate if exchange equivalence is considered 2

Resin dosage (g/L)	0,5	1	2	4	8	12	Average
K	3,77E-06	4,30E-06	2,09E-05	3,54E-05	1,05E-04	1,04E-04	4,54E-05
log K	-5,42	-5,37	-4,68	-4,45	-3,98	-3,98	-4,65

This results in a system with a much lower K value, but NOM molecules with a higher exchange equivalence. Both systems will be tried in PHREEQC.

NOM: humic acids

For humic acids the K values are determined the same way as with fulvic acids. First we consider the scenario where humic acids are monovalent, with only one active group per molecule:

Table 11: Determination of equilibrium constant K for humic acids

Resin dosage (g/L)	0,5	1	2	4	12	
NOM (mg/L)	47,15	42,98	33,61	20,94	3,79	
βNOM	0,000	0,000	0,000	0,000	0,000	
Cl- (mg/L)	6,549	2,459	4,095	5,595	5,794	
βCl	1,000	1,000	1,000	1,000	1,000	Average
K	1,80E-02	9,11E-03	2,27E-02	4,41E-02	1,33E-01	4,54E-02
log K	-1,746	-2,040	-1,644	-1,355	-0,875	-1,34

As the wateq database in PHREEQC also assumes humates to have an exchange equivalence of 2, this value will be assumed for consistency and comparison reasons. This results in the following values for K:

Table 12: K values of humate if exchange equivalence is considered 2

Resin dosage (g/L)	1	2	4	12	Average
K	6,32E-07	2,62E-06	6,97E-06	2,18E-05	7,06E-06
log K	-6,20	-5,58	-5,16	-4,66	-5,15

The table below presents an overview of the obtained K values that will be used in PHREEQC to test the viability of simulating NOM adsorption.

Table 13: K values of target anions

	K	Log K
Nitrate (NO_3^-)	1,54	0,142
Sulfate	0,12	-1,61
Fulvic acids (NOM^-)	1,65E-01	-0,93
Fulvic acids (NOM^{2-})	4,54E-05	-4,65
Humic acids (NOM^-)	4,54E-02	-1,34
Humic acids (NOM^{2-})	7,06E-06	-5,15

4.5.2 Anion adsorption in PHREEQC

Using the K values determined for nitrate, sulfate, fulvic acids and humic acids, the adsorption of the anions is modeled in PHREEQC and plotted along with the datapoints of the respective experiments. The full PHREEQC code used in this report can be found in attachment F

Nitrate

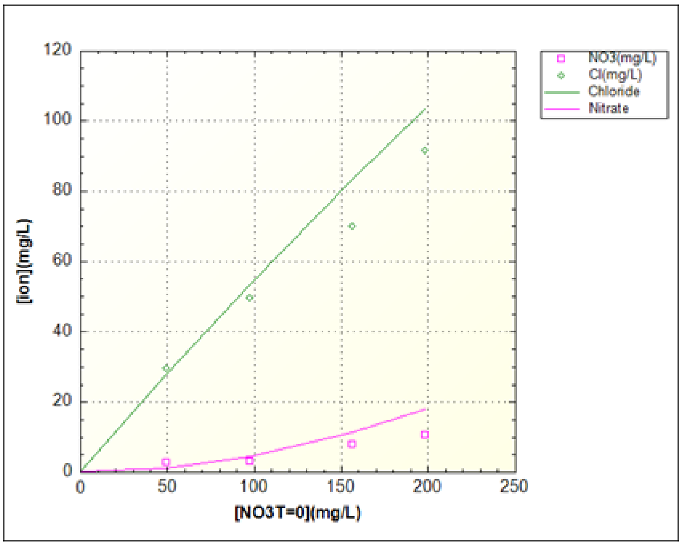


Figure 34: Nitrate and chloride concentrations from jar tests (dots) and the model with resin concentration of 20 g/L

The nitrate and chloride curves match the experimental data quite well. The amount of adsorbed nitrate is slightly underestimated for higher initial nitrate concentrations however.

Sulfate

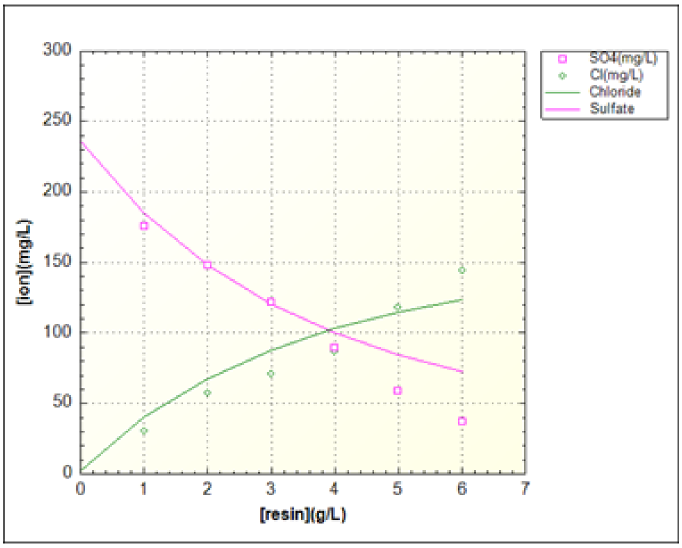


Figure 35: Sulfate and chloride concentrations from jar tests (dots) and the model for various resin concentrations

Sulfate and chloride curves follow the experimental data quite well, even though it looks like that for higher concentrations of resin the model seems to underestimate the sulfate adsorption.

Nitrate and sulfate

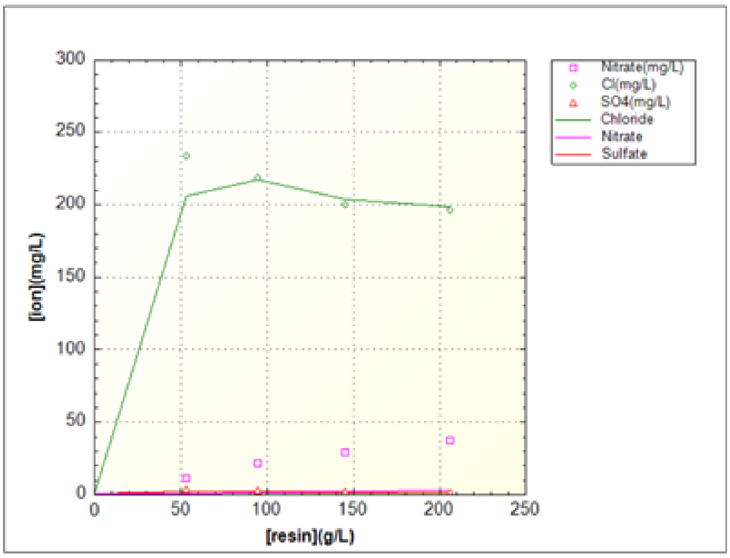


Figure 36: Sulfate, nitrate and chloride concentrations from jar tests (dots) and the model for various resin concentrations

When sulfate and nitrate are in the same system as presented in figure 36, PHREEQC overestimates the removal of both anions. All nitrate is removed in the model while the experiments still had big fractions of the original concentrations of nitrate left in the effluent.

Fulvic acids

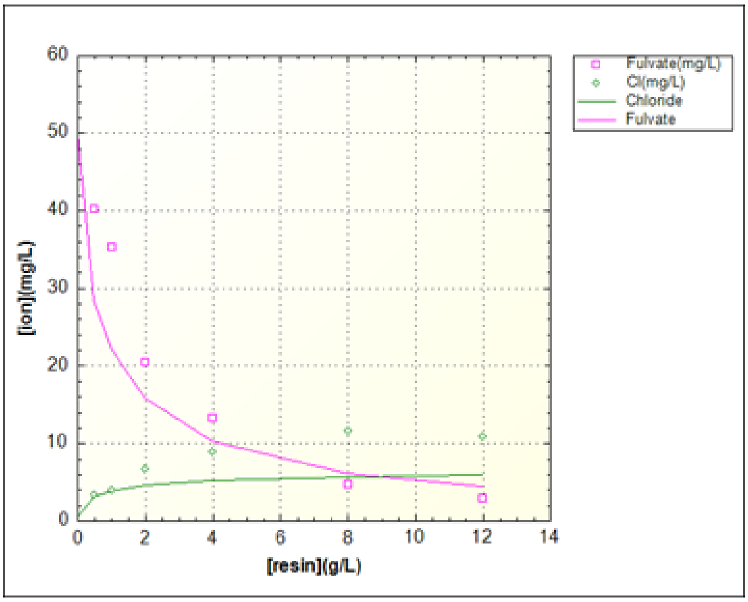


Figure 37: Anion concentrations from jar tests (dots) and the model assuming that fulvic acids are monovalent

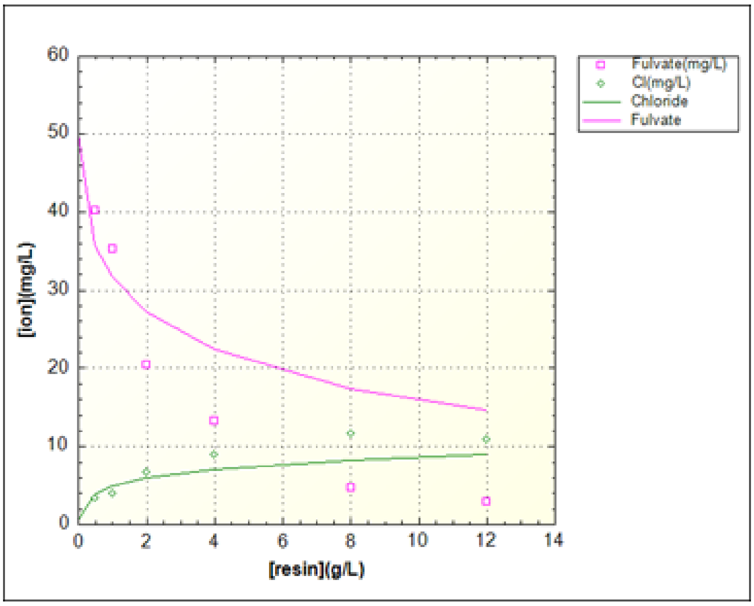


Figure 38: Anion concentrations from jar tests (dots) and the model assuming that fulvic acids are divalent

In the scenario where the fulvics are monovalent the NOM curve matches the experimental values well. The chloride released is quite underestimated however. In the other case with divalent NOM this is reversed. The chloride released is modeled well but the amount of NOM adsorbed is underestimated.

Fulvic acids and sulfate

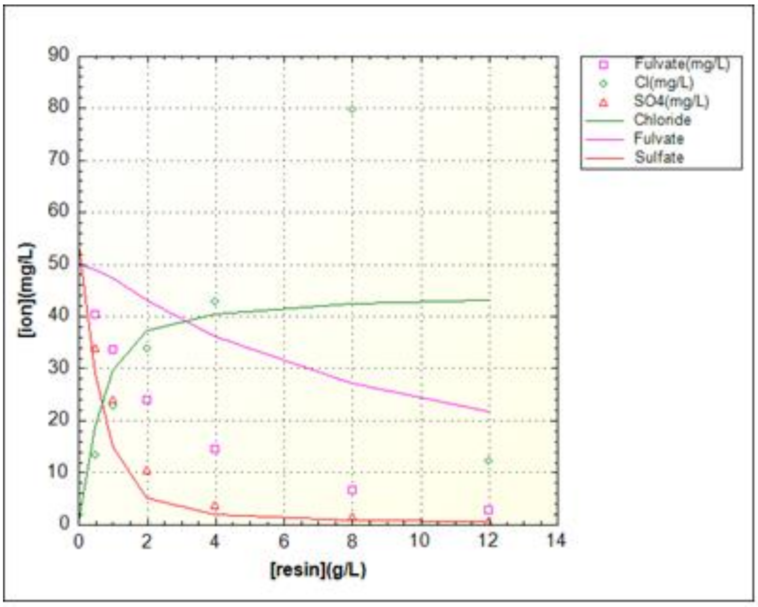


Figure 39: Anion concentrations from jar tests (dots) and the model assuming that fulvic acids are monovalent

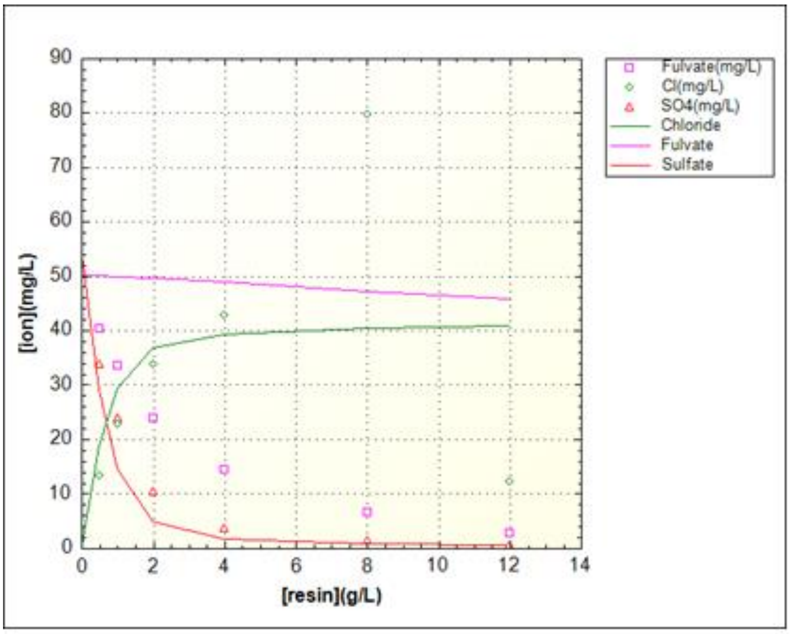


Figure 40: Anion concentrations from jar tests (dots) and the model assuming that fulvic acids are divalent

In both scenario's with NOM (mono- and divalent), the influence of the addition of sulfate is overwhelming. The sulfate takes up a big fraction of the available resin spots and especially in the case of divalent NOM the simulated adsorption of fulvic acids has basically stopped. The sulfate and chloride curves in both figures are quite accurate but the calculated NOM concentrations are overestimated. The model is assuming a hard competition of sulfate towards NOM while in the experiments these effects of competition are not as severe and the adsorption is more independently.

Humic acids

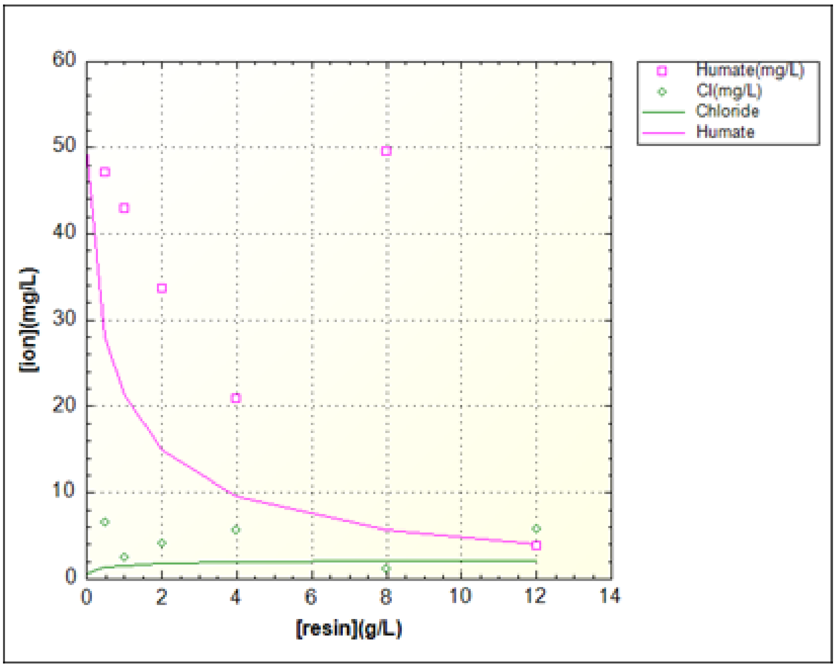


Figure 41: Anion concentrations from jar tests (dots) and the model assuming that humic acids are monovalent

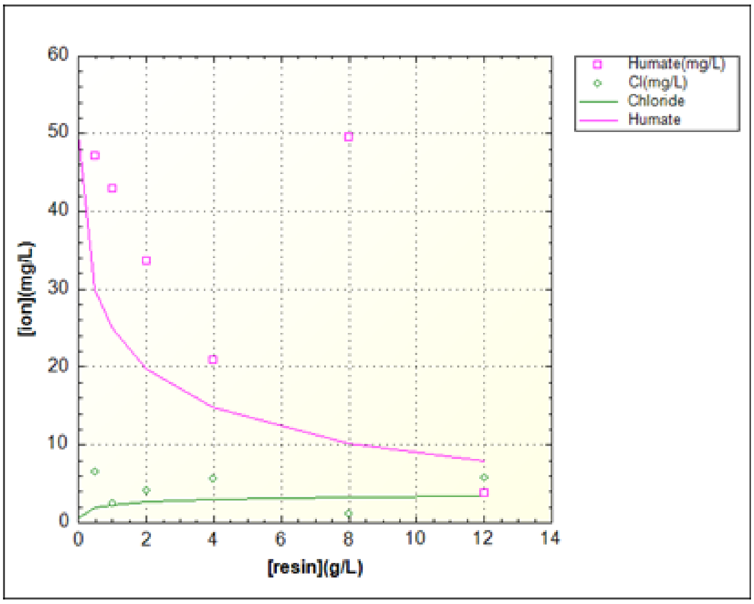


Figure 42: Anion concentrations from jar tests (dots) and the model assuming that humic acids are divalent

For both the monovalent and divalent cases the humic acids curves are quite similar. They do both overestimate the adsorption of NOM and underestimate the release of chloride, although the chloride is arguably better in the case of divalent NOM.

Humic acids and sulfate

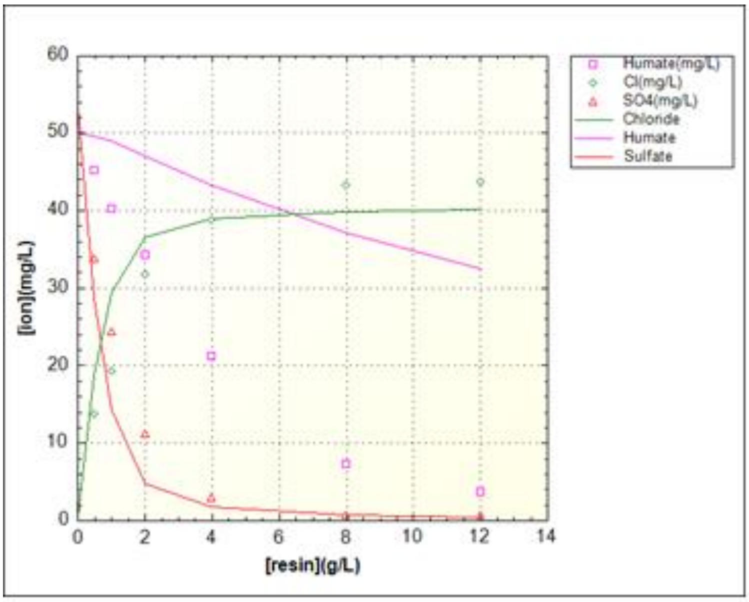


Figure 43: Anion concentrations from jar tests (dots) and the model assuming that humic acids are monovalent

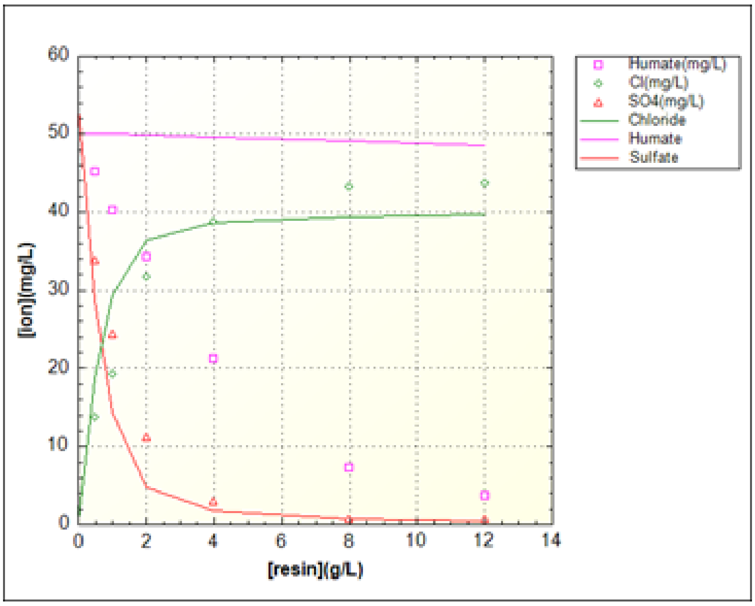


Figure 44: Anion concentrations from jar tests (dots) and the model assuming that humic acids are divalent

When sulfate gets added to a water with isolated humic acids the same thing happens as with the fulvic acids: the sulfate becomes too dominant and reduces the simulation of NOM adsorption to a minimal level.

5. Discussion

With the data obtained from the experiemental work and the PHREEQC modeling, a return to the research questions is made to answer them and evaluate the results and uncertainties that are still present.

1. *What are the ion exchange properties of NOM and how do they compare to other anions?*

NOM can be treated as an anion with a charge of around -2 at neutral pH. It has a high affinity for resin adsorption with Lewatit S5128, higher than chloride, nitrate and bicarbonate and only slightly less than sulfate.

2. *How does pH influence DOC and anion concentrations during SIX?*

The pH has a major influence on the charge of NOM molecules. At pH 8 and higher the maximum charge is present, which gradually lowers for lower pH values until there is minimal charge left on the reactive groups below pH 4. Remarkable is that at pH values of around 5 the NOM still gets removed entirely when in contact with resin concentrations of 15 g/L, the concentration used in full scale installations.

Water with high pH leads to increased counter anion release, slightly due to the increased charge of NOM which makes it exchange with more chloride, but almost entirely due to the bicarbonate adsorption that occurs at neutral and high pH ranges.

3. *How do the resin concentration and competition between anions influence NOM and anion adsorption during SIX?*

NOM adsorption is minimally influenced by competition of other anions that have high affinity such as sulfate. The adsorption is dependent on the resin concentration though, although these limitations are mostly related to the exchange capacity of the resin rather than the chemical properties of NOM.

Is it possible to predict the IEX performance with a computer model for various pH values based on the anion composition of the influent?

Modeling individual adsorption of anions is replicable in PHREEQC in a simple water matrix. The removal of target anions is in the same order of magnitude and happens at the same resin doses. The amount of chloride released is matching accurately as well. The system does however perform poorly once a system with three or more anions is introduced. The calculations of PHREEQC are majorly dependent on the chosen equilibrium constant and will overestimate the adsorption of whichever anion has the greatest selectivity at the cost of the adsorption of other anions as can be seen in figures 39,40,43 and 44. PHREEQC can be used to fit an individual data set but is unable to work as a predictive model in practice.

There can be multiple explanations as to why PHREEQC fails to simulate the IEX process in an accurate manner. Most likely for one or more of the following reasons:

- NOM is too complex to model in PHREEQC. With so many variables in the different chemical structures and reactive group combinations, the chance of outliers having too different properties is too large to assume that an average will suffice to work with in modeling.
- The size and molecular weight of the molecules is very large compared to the other anions in the system. Chloride for example is only 35.45 dalton while fulvic acids have molecular weights that can be around ten times larger (C. Rostad, J. Leenheer, 2004) while humic acids can be even a hundred times larger than that (J. Wang et al., 2009). This means that in practice it is possible that NOM can block exchange spots on the resin beads due to its size, making it harder for sulfate to exchange on the resin. The model does not incorporate the molecular weights and molecule sizes in this way and therefore it is easier for smaller molecules (such as sulfate competing with NOM) to exchange in a computer model.
- PHREEQC cannot handle a system with more than 2 exchangeable components as it is too hard to estimate the exact magnitude of domination of the most molecule species with the highest selectivity. In this case the program knows sulfate is more likely to be exchanged with chloride than fulvic acids for example but the program does not recognize a limit to this preference, so that fulvic acids will barely be adsorbed as long as sulfate is present.
- In addition to the previous bullet, an exchange reaction should have more parameters to fine-tune the total system. Currently the model is entirely dependent on equilibrium constants which makes complex matrices very one dimensional.
- The exchange capacity of resin has shown to have a big influence on the effluent water matrix. Currently the model can only recognize situations where the exchange capacity is sufficient or insufficient and will always exchange all available spots even when the limit of exchange capacity is being approached. In reality a shortage or overdose of resin will affect the anion exchange more gradually.
- Ion exchange resin is not modeled properly. Only the exchange capacity is known but the type of resin (strong/weak based/acidic) has no influence on the model. Saturation of the resin in periods of high amounts of ion exchange does not occur, the exchange capacity only acts as a maximum value but does not slow down the reactions happening which would happen due the lower amount of exchange spots making it harder for target anions to adsorb.

6. Conclusions

While the results of the PHREEQC modeling has not given the promising prediction model that was expected, the experimental work has definitely given valuable insights in especially the chemical properties of natural organic matter. The relation with pH, the chloride exchange capacity and the selectivity are known accurate enough to compare these molecules with ion exchange competitors such as sulfate and nitrate.

Jar tests

The jar tests with softened lake Ijssel water show that removal of natural organic matter is unaffected by pH changes. The bench scale tests show that the resin has a preference for sulfate over natural organic matter, as only half of the NOM is adsorbed when the sulfate is already fully adsorbed.
Different pH values influence the chloride concentrations in the effluent as shown in figures 22 and 23, due to the amount of bicarbonate in the water at neutral and high pH, which exchanges with chloride on the resin.

Isolated nitrate and sulfate removal with Lewatit S5128 shows a very high selectivity for sulfate and a selectivity for nitrate that is in the order of magnitude of counter anion chloride. Sulfate has a higher selectivity than nitrate and will only leave a sufficient amount of concentration left in the effluent at low resin concentrations to be able to calculate equilibrium constants.

Natural organic matter has shown to have a counter anion exchange equivalence of 2 to 8 mol chloride per NOM molecule. This high capacity suggests a high selectivity which is confirmed by the fact that addition of sulfate barely affects NOM adsorption. Like with the lake Ijssel jar tests, the main effect of pH on the effluent is the chloride concentrations, which increase for higher pH values.

Titrations

The amounts of carboxylic acids in the samples are in the order of magnitude with other NOM samples found by J. Ritchie and E. Perdue (2002). It is noticeable that the humic acids sample contains the most amount of carboxyl groups. The amount of phenolic activity seems to be minimal in the samples (table 5), in regular fulvic acid samples it is not present at all.

These titrations have given useful insights about the charge of NOM over most of the pH range. The charge of NOM is close to its highest value at pH 8 and higher, while the charge becomes negligible at charges below 4, making the pH range between 4 and 8 the range that should be best monitored when it comes to potential NOM charge changes.

Recommendations

Although PHREEQC under current circumstances is not able to predict kinetics within complex water matrices, there is potential for improvements. Several recommended changes and additions are presented below:

- The most obvious improvement the PHREEQC model needs is to be less dependent on the equilibrium constants in systems with three or more anions. To achieve this the K values could be re-determined by more experiments that run on a larger scale. Additionally other factors within the model that can affect the calculations should be recalibrated, such as the resin exchange capacity, the definition of NOM and the relation between chloride and the resin.
- Jar tests with isolated (bi)carbonate can be done to determine the equilibrium constant and be able to better implement this essential anion into the system
- Implement pH changes into the model. It is known that NOM adsorption is unaffected by pH changes so the effects on bicarbonate concentrations should be the determining factor into whether pH correctly alters the system in the model.
- Perform jar tests with anions that are not tested currently but can occur more frequently in waters treated by anion exchange such as phosphate. This is not an absolute necessity to improve the model directly but other chemicals that are relevant in other waters than studied in this report might provide new challenges that need to be tackled.
- More data about NOM adsorption needs to be collected to be able to reliably predict behavior of unknown NOM samples. The NOM samples used in this research showed several differences in chemical properties such as molecule size, DOC/NOM ratio, chloride exchange equivalence and sensitivity to pH changes. In practice NOM modeling would most likely require knowledge about the chemical properties of NOM as the differences between different NOM samples are too varying.
- The resin must be defined more precisely in the model than a fictional cation Z^+. There are numerous types of resin that work on different pH ranges, are loaded with different counter-ions and have different exchange capacities. Each of those properties should be reflected in the PHREEQC model to advance from the current system where only the maximum exchange capacity is known and saturation of the resin has no effect until the arbitrary limit is reached.

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Attachment A: SIX influent jar test results

SIX influent with increased pH

Jar 1

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	8,17	21,6	0,4	83,2	149
2			0,32	86,3	184
5			0,265	88,5	208
10			0,186	91,8	218
15			0,148	93,4	223
20			0,113	94,9	234
30			0,083	96,3	245
45	7,88	22,2	0,07	96,8	245

Jar 2

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	8,41	21,6	0,436	81,8	129
2			0,325	86,1	219
5			0,259	88,8	203
10			0,185	91,8	222
15			0,138	93,8	228
20			0,107	95,2	242
30			0,082	96,2	244
45	7,94	22,2	0,073	96,7	226

Jar 3

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	8,70	21,6	0,419	82,4	143
2			0,334	85,7	171
5			0,263	88,6	236
10			0,193	91,4	214
15			0,138	93,8	234
20			0,113	94,9	232
30			0,08	96,4	229
45	8,05	22,3	0,075	96,6	247

Jar 4

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	9,17	21	0,416	82,6	132
2			0,322	86,2	176
5			0,255	88,9	229
10			0,185	91,8	238
15			0,144	93,6	258
20			0,115	94,8	243
30			0,082	96,3	272
45	8,24	21,6	0,078	96,5	218

Jar 5

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	9,84	21	0,405	83,0	142
2			0,308	86,8	175
5			0,24	89,5	222
10			0,174	92,3	238
15			0,129	94,2	254
20			0,104	95,3	241
30			0,078	96,5	274
45	8,67	21,5	0,067	97,0	220

Jar 6

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	10,9	21,1	0,406	82,9	145
2			0,309	86,7	204
5			0,25	89,1	275
10			0,181	92,0	284
15			0,138	93,8	304
20			0,11	95,1	353
30			0,083	96,2	317
45	10,12	21,7	0,071	96,8	301

SIX influent with increased pH

Jar 1

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	8,01	21,4	0,382	83,9	183
2			0,288	87,6	204
5			0,229	90,0	229
10			0,166	92,6	239
15			0,121	94,6	267
20			0,097	95,6	232
30			0,078	96,5	232
45	7,87	21,8	0,063	97,1	261

Jar 2

Time (min)	pH	T(°C)	UVA	UVT (%)	Cl- (mg/L)
0	7,7	21,3	0,376	84,1	168
2			0,301	87,1	211
5			0,234	89,8	217
10			0,165	92,7	239
15			0,12	94,6	240
20			0,103	95,4	233
30			0,076	96,6	251
45	7,85	21,7	0,063	97,1	257

Jar 3

Time (min)	**pH**	**T(°C)**	**UVA**	**UVT (%)**	**Cl- (mg/L)**
0	7,24	21,4	0,376	84,1	176
2			0,308	86,8	198
5			0,229	90,0	215
10			0,167	92,6	238
15			0,117	94,8	244
20			0,095	95,7	231
30			0,07	96,8	251
45	7,57	21,9	0,063	97,1	246

Jar 4

Time (min)	**pH**	**T(°C)**	**UVA**	**UVT (%)**	**Cl- (mg/L)**
0	6,96	21,6	0,382	83,9	184
2			0,294	87,3	210
5			0,234	89,8	206
10			0,163	92,8	227
15			0,123	94,5	216
20			0,098	95,6	236
30			0,08	96,4	216
45	7,41	22,6	0,061	97,2	257

Jar 5

Time (min)	**pH**	**T(°C)**	**UVA**	**UVT (%)**	**Cl-(mg/L)**
0	6,31	21,6	0,376	84,1	197
2			0,298	87,2	220
5			0,228	90,0	209
10			0,163	92,8	237
15			0,127	94,3	217
20			0,099	95,5	227
30			0,071	96,8	226
45	6,81	22,6	0,057	97,4	232

Jar 6

Time (min)	**pH**	**T(°C)**	**UVA**	**UVT (%)**	**Cl- (mg/L)**
0	5,03	21,7	0,38	83,9	221
2			0,297	87,2	227
5			0,232	89,9	218
10			0,16	92,9	236
15			0,129	94,2	273
20			0,101	95,5	245
30			0,077	96,5	232
45	6,08	22,6	0,065	97,1	245

Attachment B: SIX influent bench scale test results

SIX influent with increased pH

pH	T(°C)	Time (min)	UVA	UVT (%)	DOC (mg/L)	Cl- (mg/L)	$HCO3^{-}$ (mg/L)	$CO3^{2-}$ (mg/L)	$NO3^{-}$ (mg/L)	$SO4^{2-}$ (mg/L)
8	14,1	0	0,389	83,60	4,4	168	129,1	0	1,7	46,2
10,91	14,9	0	0,387	83,68	4,6	169	-32,0	119,6	1,5	43,9
		5	0,191	91,58	4,2	257	-7,9	59,5	0,80	17,1
		10	0,161	92,85	3,9	287	-3,3	40,8	0,66	5,03
		20	0,116	94,80	3,2	302	0,7	29,1	0,67	1,72
		30	0,084	96,21	3,3	305	-1,3	27,5	0,70	1,27
	15,5	45	0,068	96,92	2,8	350	2,7	25,9	0,77	1,13

SIX influent with decreased pH

pH	T(°C)	Time (min)	UVA	UVT (%)	DOC (mg/L)	Cl- (mg/L)	$HCO3^{-}$ (mg/L)	$CO3^{2-}$ (mg/L)	$NO3^{-}$ (mg/L)	$SO4^{2-}$ (mg/L)
8	14,9	0	0,384	83,79	4,6	169	128,0	0	1,43	45,2
4,61	14,9	0	0,384	83,79	4,5	248	0	0	1,28	45,4
		5	0,233	89,83	4,3	266	7,0	0	0,70	15,6
		10	0,194	91,45	3,1	271	9,0	0	0,59	8,14
		20	0,136	93,93	2,9	270	11,1	0	0,69	1,17
		30	0,104	95,32	2,8	273	11,5	0	0,52	0,422
	15,8	45	0,085	96,16	2,6	274	11,4	0	0,59	1,68

Attachment C: Anion spiking jar test results

Sulfate				
SO4 (2-) (mg/L)	100	150	200	250
Na2SO4 (mg) dosage per 1,5 L	221,80	332,70	443,60	554,50
pH T= 0	7,02	6,73	6,7	6,7
pH T= 60 min	7,34	7,25	7,4	7,57
SO4(2-) (mg/L) T=0	109	151	220	265
SO4(2-) (mg/L) T=60 min	0	0	0	0
Cl- (mg/L) T=60 min	74	98,5	121	160

Sulfate						
Resin dosage (g/L)	5	10	15	20	25	30
SO4(2-) (mg/L) T=0	164,6	164,6	164,6	164,6	164,6	164,6
SO4(2-) (mg/L) T=45 min	0	0	0	0	0	0
Cl- (mg/L) T=0	2,25	2,25	2,25	2,25	2,25	2,25
Cl- (mg/L) T=45 min	113	127	123	115	105	112
pH T=0	5,64	5,64	5,64	5,64	5,64	5,64
pH T=45 min	7,54	7,5	7,55	7,5	7,6	7,56

Sulfate						
Resin dosage (g/L)	1	2	3	4	5	6
SO4(2-) (mg/L) T=0	236	236	236	236	236	236
SO4(2-) (mg/L) T=45 min	176	148	122	89,3	58,8	37
Cl- (mg/L) T=0	2,05	2,05	2,05	2,05	2,05	2,05
Cl- (mg/L) T=45 min	30	57,1	70,5	86,5	118	144
pH T=0	5,66	5,66	5,66	5,66	5,66	5,66
pH T=45 min	6,19	6,42	6,51	6,72	6,85	6,82

Nitrate				
NO3 - (mg/L)	50	100	150	200
NaNO3 (mg) dosage per 1,5 L	102,81	205,62	308,42	411,23
pH T= 0	6,35	6,21	6,23	6,17
pH T= 60 min min	7,32	7,27	7,33	7,44
NO3- (mg/L) T=0	49,5	97,2	156,5	198,4
NO3- (mg/L) T=60 min min	2,76	2,99	7,88	10,7
Cl- (mg/L) T=60 min	29,5	49,6	70	91,6

Sulfate + nitrate				
SO4(2-) (mg/L)	250	200	150	100
NO3 - (mg/L)	50	100	150	200
Na2SO4 (mg) dosage per 1.5 L	554,50	443,60	332,70	221,80
NaNO3 (mg) dosage per 1,5 L	102,81	205,62	308,42	411,23
pH T= 0	6,4	6,25	6,13	5,84
pH T= 60 min	7,96	7,98	7,95	7,92
SO4(2-) (mg/L) T=0	260	212	165	113
NO3- (mg/L) T=0	50,4	101,8	151,2	205,2
SO4(2-) (mg/L) T=60 min	0	0	0	0
NO3- (mg/L) T=60 min	5,58	10,01	13,9	17,9
Cl- (mg/L) T=60 min	201	201	186	184

Sulfate + nitrate (lower conc.)				
SO4(2-) (mg/L)	35	70	105	140
NO3 - (mg/L)	26	52	78	104
Na2SO4 (mg) dosage per 1.5 L	77,63	155,26	232,89	310,52
NaNO3 (mg) dosage per 1,5 L	53,46	106,92	160,38	213,84
pH T= 0	6,71	6,29	6,13	5,74
pH T= 60 min				
SO4(2-) (mg/L) T=0	21,6	64,1	109	155
NO3- (mg/L) T=0	26,9	50,8	78,4	109,8
SO4(2-) (mg/L) T=60 min	0	0	0	0
NO3- (mg/L) T=60 min	1,25	3,98	6,86	10,6
Cl- (mg/L) T=60 min	37,1	64,8	89,1	104

Sulfate + nitrate (HWL)				
SO4(2-) (mg/L)	250	200	150	100
NO3 - (mg/L)	50	100	150	200
Na2SO4 (mg) dosage per 2 L	739,33	591,46	443,60	295,73
NaNO3 (mg) dosage per 2 L	137,08	274,15	411,23	548,31
pH T= 0	6,3	6,19	6,1	6,12
pH T= 45 min	7,01	7,14	7,15	7,26
SO4(2-) (mg/L) T=0	240,28	220,57	158,78	106,87
NO3- (mg/L) T=0	44,2	97,21	132,31	194,03
HCO3- (mg/L) T=0	2,88	2,62	2,55	2,5
SO4(2-) (mg/L) T=45 min	3,66	4,49	1,33	1,34
NO3- (mg/L) T=45 min	9,31	20,3	23,38	33,75
HCO3- (mg/L) T=45 min	8,75	8,82	8,2	7,95
Cl- (mg/L) T=45 min	200,75	195,7	174,02	168,63

Sulfate + nitrate pH 8 (HWL)				
SO4(2-) (mg/L)	250	200	150	100
NO3 - (mg/L)	50	100	150	200
Na2SO4 (mg) dosage per 2 L	739,33	591,46	443,60	295,73
NaNO3 (mg) dosage per 2 L	137,08	274,15	411,23	548,31
pH T= 0	8,87	8,88	8,91	8,78
pH T= 60 min	7,6	7,62	7,52	7,47
SO4(2-) (mg/L) T=0	239,01	221,76	165,36	110,60
NO3- (mg/L) T=0	53,75	94,99	145,52	206,12
HCO3- (mg/L) T=0	9,08	9,03	8,91	8,83
SO4(2-) (mg/L) T=45 min	3,15	2,210	2,13	0,99
NO3- (mg/L) T=45 min	10,76	21,06	28,42	37,13
HCO3- (mg/L) T=45 min	11,4	11,15	10,58	10,55
Cl- (mg/L) T=45 min	233,32	218,21	199,99	196,26

Attachment D: NOM spiking jar test results

Fulvic acid (Jadis additiva)

NOM conc (mg/L)	50	100	150
pH T=0	6,910	7,19	7,8
pH T=45 min	6,11	6,35	6,56
UVA T=0	3,046	2,916 (2x vdnd)	2,889 (3x vdnd)
UVT T=0 (%)	24,592	6,817	1,848
UVA T=45 min	0,016	0,057	0,126
UVT T=45 min (%)	99,27	97,41	94,36
SO4(2-) (mg/L) T=0	0	0	1,34
SO4(2-) (mg/L) T=45 min	0	0	0
HCO3- (mg/L) T=0	9,86	16,4	23,66
HCO3- (mg/L) T=45 min	2,73	3,11	3,5
CO2(2-) (mg/L) T=0	0	0	0
CO2(2-) (mg/L) T=45 min	0	0	0
DOC (mg/L) T=0	16,56	30,73	47,58
DOC (mg/L) T=45 min	0,7055	0,8998	1,136
Cl- (mg/L) T=0	0,807	1,601	2,412
Cl- (mg/L) T=45 min	8,542	14,817	23,900

Fulvic acid (PWN fulvic)

NOM conc (mg/L)	50	100	150
pH T=0	3,9	3,62	3,53
pH T=45 min	3,91	3,56	3,33
UVA T=0	0,893	1,941	3,003
UVT T=0 (%)	12,79	1,15	0,10
UVA T=45 min	0,042	0,055	0,105
UVT T=45 min (%)	90,78	88,10	78,52
SO4(2-) (mg/L) T=0	2,44576	4,81079	6,40113
SO4(2-) (mg/L) T=45 min	0,35851	0,29111	0,19887
HCO3- (mg/L) T=0	0	0	0
HCO3- (mg/L) T=45 min	0	0	0
CO2(2-) (mg/L) T=0	0	0	0
CO2(2-) (mg/L) T=45 min	0	0	0
DOC (mg/L) T=0	26,07	48,48	75,33
DOC (mg/L) T=45 min	0,9506	2,066	4,275
Cl- (mg/L) T=0	1,01576	1,76151	2,38142
Cl- (mg/L) T=45 min	4,90342	11,09827	20,10651

Humic acid (PWN humic)

NOM conc (mg/L)	50	100	150
pH T=0	4,32	4,1	3,96
pH T=45 min	4,27	3,97	3,76
UVA T=0	0,96	1,75	2,59
UVT T=0 (%)	11,04	1,77	0,26
UVA T=45 min	0,087	0,202	0,32
UVT T=45 (%)	81,85	62,81	48,08
SO4(2-) (mg/L) T=0	2,926	3,49	4,08
SO4(2-) (mg/L) T=45 min	1,025	1,62	2,04
HCO3- (mg/L) T=0	0	0	0
HCO3- (mg/L) T=45 min	0	0	0
CO2(2-) (mg/L) T=0	0	0	0
CO2(2-) (mg/L) T=45 min	0	0	0
DOC (mg/L) T=0	17,62	27,34	37,47
DOC (mg/L) T=45 min	2,64	9,36	8,35
Cl- (mg/L) T=0	3,4	2,77	3,23
Cl- (mg/L) T=45 min	2,69	5,11	7,55

Fulvic acid (Watergroep)

NOM conc (mg/L)	100
pH T=0	3,69
pH T=45 min	3,65
UVA T=0	1,55
UVT T=0 (%)	2,79
UVA T=45 min	0,065
UVT T=45 min (%)	86,10
SO4(2-) (mg/L) T=0	0
SO4(2-) (mg/L) T=45 min	0
HCO3- (mg/L) T=0	0
HCO3- (mg/L) T=45 min	0
CO2(2-) (mg/L) T=0	0
CO2(2-) (mg/L) T=45 min	0
DOC (mg/L) T=0	61,72
DOC (mg/L) T=45 min	0,90
Cl- (mg/L) T=0	1,8
Cl- (mg/L) T=45 min	8

NOM with pH increased to neutral range

	PWN Fulvics		**PWN Humic**		**Watergroep Fulvic**	
NOM conc (mg/L)	100	150	100	150	100	150
pH T=0	3,5	3,4	3,78	3,8	3,56	3,44
mL of 0,1 M NaOH added	10	15	5	6	9	13
pH T=0 (corrected)	7,5	7,5	7,9	7	7,9	7,6
pH T=45 min						
SO4(2-) (mg/L) T=0	0.286	0.291	0.276	0.281	0.287	0.377
SO4(2-) (mg/L) T=45 min	0	0	0	0	0	0
DOC (mg/L) T=0	47,5	70,26	26,8	35,81	46,5	68,04
DOC (mg/L) T=45 min	2,13	1,85	5,34	8,50	1,77	2,5
Cl- (mg/L) T=0	0.94	0.50	0.52	0.38	0.37	0.39
Cl- (mg/L) T=45 min	19.98	29.27	5.77	11.04	17.71	

PWN fulvics with low resin concentrations

NOM (mg/L) T=0	50	50	50	50	50	50
Resin conc (g/L)	0,5	1	2	4	8	12
DOC (mg/L) T=0	22,96	22,96	22,96	22,96	22,96	22,96
DOC (mg/L) T=45	18,45	16,23	9,38	6,11	2,17	1,31
NOM (mg/L) T=45	40,18	35,34	20,43	13,31	4,73	2,85
SO4(2-) (mg/L) T=0	0,606	0,606	0,606	0,606	0,606	0,606
SO4(2-) (mg/L) T=45	0,594	0,589	0,588	0,577	0,581	0,569
Cl- (mg/L) T=0	0,461	0,461	0,461	0,461	0,461	0,461
Cl- (mg/L) T=45	3,387	3,954	6,6	8,877	11,634	10,806
Na+ (mg/L) T=0	9,231	9,231	9,231	9,231	9,231	9,231
Na+ (mg/L) T=45	9,427	9,581	9,97	9,826	11,054	10,303

PWN fulvics with sulfate and low resin concentrations

NOM (mg/L) T=0	50	50	50	50	50	50
Resin conc (g/L)	0,5	1	2	4	8	12
DOC (mg/L) T=0	24,02	24,02	24,02	24,02	24,02	24,02
DOC (mg/L) T=45	19,41	16,11	11,52	7	3,17	1,3
NOM (mg/L) T=45	40,40	33,53	23,98	14,57	6,60	2,71
SO4(2-) (mg/L) T=0	53,746	53,746	53,746	53,746	53,746	53,746
SO4(2-) (mg/L) T=45	33,793	23,876	10,505	3,741	1,353	0,57
Cl- (mg/L) T=0	0,469	0,469	0,469	0,469	0,469	0,469
Cl- (mg/L) T=45	13,265	22,847	33,739	42,89	79,366	12,174
Na+ (mg/L) T=0	40,578	40,578	40,578	40,578	40,578	40,578
Na+ (mg/L) T=45	35,987	36,91	36,269	37,465	61,636	11,827

PWN humics with low resin concentrations

NOM (mg/L) T=0	50	50	50	50	50	50
Resin conc (g/L)	0,5	1	2	4	8	12
DOC (mg/L) T=0	22,09	22,09	22,09	22,09	22,09	22,09
DOC (mg/L) T=45	20,83	18,99	14,85	9,25	21,9	1,675
NOM (mg/L) T=45	47,15	42,98	33,61	20,94	49,57	3,79
SO4(2-) (mg/L) T=0	0,591	0,591	0,591	0,591	0,591	0,591
SO4(2-) (mg/L) T=45	0,6	0,576	0,572	0,569	0,584	0,567
Cl- (mg/L) T=0	0,435	0,435	0,435	0,435	0,435	0,435
Cl- (mg/L) T=45	6,549	2,459	4,095	5,595	1,074	5,794
Na+ (mg/L) T=0	5,501	5,501	5,501	5,501	5,501	5,501
Na+ (mg/L) T=45	10,58	5,625	6,529	6,519	6,184	6,081

PWN humics with sulfate and low resin concentrations

NOM (mg/L) T=0	50	50	50	50	50	50
Resin conc (g/L)	0,5	1	2	4	8	12
DOC (mg/L) T=0	24,49	24,49	24,49	24,49	24,49	24,49
DOC (mg/L) T=45	22,11	19,73	16,78	10,4	3,57	1,8
NOM (mg/L) T=45	45,14	40,28	34,26	21,23	7,29	3,67
SO4(2-) (mg/L) T=0	53,398	53,398	53,398	53,398	53,398	53,398
SO4(2-) (mg/L) T=45	33,836	24,309	11,152	2,848	0,673	0,585
Cl- (mg/L) T=0	0,414	0,414	0,414	0,414	0,414	0,414
Cl- (mg/L) T=45	13,673	19,304	31,691	38,695	43,258	43,629
Na+ (mg/L) T=0	33,05	33,05	33,05	33,05	33,05	33,05
Na+ (mg/L) T=45	33,755	32,938	34,413	33,204	34,356	34,264

Attachment E: Titrations results

PWN fulvic acids

Added 0,1 M HCl (mL)	pH	Total volume (mL)
0	3,14	50
1	2,58	51

Addition of HCl to lower starting pH below 2,7. Titration with NaOH below

Added 0,1 M NaOH (mL)	pH
0	2,58
0,006	2,58
0,012	2,58
0,018	2,58
0,024	2,58
0,03	2,58
0,036	2,58
0,042	2,58
0,048	2,58
0,054	2,58
0,06	2,58
0,066	2,58
0,072	2,58
0,078	2,58
0,084	2,58
0,09	2,58
0,096	2,58
0,102	2,58
0,108	2,58
0,114	2,58
0,12	2,58
0,126	2,58
0,132	2,58
0,138	2,58
0,144	2,59
0,15	2,59
0,156	2,59
0,162	2,59
0,168	2,59
0,174	2,6
0,18	2,6
0,186	2,6
0,192	2,6
0,198	2,6
0,204	2,61
0,21	2,61
0,216	2,61
0,222	2,61
0,228	2,63
0,234	2,62
0,24	2,62
0,246	2,62
0,252	2,62
0,258	2,64
0,264	2,63
0,27	2,63
0,276	2,63
0,282	2,64
0,288	2,64
0,294	2,64
0,3	2,65
0,306	2,65
0,312	2,66
0,318	2,66
0,324	2,66
0,33	2,66
0,336	2,66
0,342	2,66
0,348	2,67
0,354	2,67
0,36	2,68
0,366	2,68
0,372	2,68
0,378	2,68
0,384	2,68
0,39	2,68
0,396	2,69
0,402	2,69
0,408	2,69
0,414	2,7
0,42	2,7
0,426	2,7
0,432	2,7
0,438	2,7
0,444	2,71
0,45	2,71
0,456	2,71
0,462	2,71
0,468	2,73
0,474	2,72
0,48	2,72
0,486	2,72
0,492	2,72
0,498	2,74
0,504	2,74
0,51	2,74
0,516	2,73
0,522	2,74
0,528	2,75
0,534	2,75
0,54	2,75
0,546	2,76
0,552	2,76
0,558	2,76
0,564	2,76
0,57	2,77
0,576	2,77
0,582	2,77
0,588	2,77
0,594	2,77
0,6	2,78
0,606	2,78

0,612	2,78
0,618	2,8
0,624	2,8
0,63	2,8
0,636	2,8
0,642	2,81
0,648	2,81
0,654	2,81
0,66	2,81
0,666	2,81
0,672	2,83
0,678	2,83
0,684	2,82
0,69	2,83
0,696	2,84
0,702	2,84
0,708	2,84
0,714	2,84
0,72	2,85
0,726	2,85
0,732	2,85
0,738	2,85
0,744	2,87
0,75	2,87
0,756	2,87
0,762	2,87
0,768	2,88
0,774	2,88
0,78	2,88
0,786	2,88
0,792	2,89
0,798	2,9
0,804	2,9
0,81	2,9
0,816	2,91
0,822	2,92
0,828	2,91
0,834	2,91
0,84	2,93
0,846	2,93
0,852	2,93
0,858	2,93
0,864	2,95
0,87	2,95
0,876	2,95
0,882	2,95

0,888	2,97
0,894	2,97
0,9	2,97
0,906	2,97
0,912	2,99
0,918	2,98
0,924	2,98
0,93	2,98
0,936	2,99
0,942	3
0,948	3
0,954	3
0,96	3,02
0,966	3,02
0,972	3,02
0,978	3,02
0,984	3,04
0,99	3,04
0,996	3,04
1,002	3,06
1,008	3,06
1,014	3,06
1,02	3,06
1,026	3,07
1,032	3,08
1,038	3,08
1,044	3,08
1,05	3,1
1,056	3,1
1,062	3,1
1,068	3,1
1,074	3,12
1,08	3,12
1,086	3,12
1,092	3,12
1,098	3,15
1,104	3,15
1,11	3,15
1,116	3,17
1,122	3,17
1,128	3,17
1,134	3,19
1,14	3,19
1,146	3,19
1,152	3,19
1,158	3,2

1,164	3,22
1,17	3,22
1,176	3,22
1,182	3,25
1,188	3,24
1,194	3,24
1,2	3,24
1,206	3,27
1,212	3,27
1,218	3,27
1,224	3,28
1,23	3,29
1,236	3,3
1,242	3,3
1,248	3,31
1,254	3,33
1,26	3,33
1,266	3,34
1,272	3,36
1,278	3,36
1,284	3,36
1,29	3,39
1,296	3,39
1,302	3,39
1,308	3,4
1,314	3,42
1,32	3,42
1,326	3,44
1,332	3,45
1,338	3,45
1,344	3,45
1,35	3,49
1,356	3,49
1,362	3,49
1,368	3,52
1,374	3,53
1,38	3,53
1,386	3,53
1,392	3,56
1,398	3,56
1,404	3,56
1,41	3,59
1,416	3,6
1,422	3,6
1,428	3,6
1,434	3,65

1,44	3,64
1,446	3,64
1,452	3,68
1,458	3,69
1,464	3,69
1,47	3,73
1,476	3,73
1,482	3,73
1,488	3,73
1,494	3,76
1,5	3,78
1,506	3,78
1,512	3,78
1,518	3,83
1,524	3,83
1,53	3,83
1,536	3,88
1,542	3,88
1,548	3,88
1,554	3,95
1,56	3,95
1,566	3,95
1,572	3,95
1,578	4,03
1,584	4,03
1,59	4,03
1,596	4,03
1,602	4,11
1,608	4,13
1,614	4,16
1,62	4,18
1,626	4,18
1,632	4,19
1,638	4,2
1,644	4,22
1,65	4,25
1,656	4,26
1,662	4,3
1,668	4,31
1,674	4,32
1,68	4,34
1,686	4,36
1,692	4,38
1,698	4,39
1,704	4,41
1,71	4,44
1,716	4,49
1,722	4,49
1,728	4,5
1,734	4,53
1,74	4,56
1,746	4,6
1,752	4,64
1,758	4,66
1,764	4,67
1,77	4,73
1,776	4,75
1,782	4,76
1,788	4,79
1,794	4,82
1,8	4,84
1,806	4,85
1,812	4,88
1,818	4,93
1,824	5
1,83	5,03
1,836	5,04
1,842	5,06
1,848	5,07
1,854	5,08
1,86	5,1
1,866	5,2
1,872	5,23
1,878	5,24
1,884	5,27
1,89	5,3
1,896	5,35
1,902	5,38
1,908	5,44
1,914	5,44
1,92	5,5
1,926	5,53
1,932	5,62
1,938	5,65
1,944	5,67
1,95	5,72
1,956	5,77
1,962	5,78
1,968	5,83
1,974	5,87
1,98	5,99
1,986	6,04
1,992	6,08
1,998	6,11
2,004	6,13
2,01	6,25
2,016	6,33
2,022	6,39
2,028	6,43
2,034	6,48
2,04	6,57
2,046	6,6
2,052	6,7
2,058	6,82
2,064	6,86
2,07	6,96
2,076	7,15
2,082	7,3
2,088	7,37
2,094	7,49
2,1	7,63
2,106	7,73
2,112	7,8
2,118	7,92
2,124	8,09
2,13	8,23
2,136	8,31
2,142	8,37
2,148	8,41
2,154	8,43
2,16	8,55
2,166	8,64
2,172	8,69
2,178	8,74
2,184	8,82
2,19	8,87
2,196	8,93
2,202	9
2,208	9,03
2,214	9,05
2,22	9,06
2,226	9,09
2,232	9,1
2,238	9,2
2,244	9,27
2,25	9,28
2,256	9,29
2,262	9,31

2,268	9,35
2,274	9,42
2,28	9,44
2,286	9,45
2,292	9,47
2,298	9,48
2,304	9,52
2,31	9,55
2,316	9,58
2,322	9,59
2,328	9,61
2,334	9,63
2,34	9,64
2,346	9,69
2,352	9,68
2,358	9,68
2,364	9,68
2,37	9,71
2,376	9,73
2,382	9,75
2,388	9,79
2,394	9,81
2,4	9,82
2,406	9,87
2,412	9,88
2,418	9,89
2,424	9,92
2,43	9,93
2,436	9,94
2,442	9,96
2,448	10
2,454	10,02
2,46	10,02
2,466	10,04
2,472	10,07
2,478	10,08
2,484	10,09
2,49	10,1
2,496	10,11
2,502	10,13
2,508	10,15
2,514	10,17
2,52	10,16
2,526	10,18
2,532	10,21
2,538	10,2
2,544	10,21
2,55	10,24
2,556	10,27
2,562	10,27
2,568	10,29
2,574	10,3
2,58	10,3
2,586	10,3
2,592	10,31
2,598	10,32
2,604	10,36
2,61	10,36
2,616	10,36
2,622	10,37
2,628	10,39
2,634	10,39
2,64	10,4
2,646	10,4
2,652	10,43
2,658	10,43
2,664	10,44
2,67	10,46
2,676	10,45
2,682	10,47
2,688	10,48
2,694	10,48
2,7	10,49
2,706	10,5
2,712	10,52
2,718	10,53
2,724	10,52
2,73	10,53
2,736	10,54

PWN humic acids

Added 0,1 M HCl (mL)	pH	Total volume (mL)
0	3,43	50
1	2,64	51

Addition of HCl to lower starting pH below 2,7. Titration with NaOH below

Added 0,1 M NaOH (mL)	pH
0	2,64
0,006	2,64
0,012	2,64
0,018	2,64
0,024	2,64
0,03	2,64
0,036	2,64
0,042	2,66
0,048	2,69
0,054	2,7
0,06	2,7
0,066	2,7
0,072	2,72
0,078	2,73
0,084	2,73
0,09	2,73
0,096	2,73
0,102	2,73
0,108	2,73
0,114	2,76
0,12	2,76
0,126	2,76
0,132	2,76
0,138	2,76
0,144	2,76
0,15	2,77
0,156	2,77
0,162	2,77
0,168	2,77
0,174	2,77
0,18	2,79
0,186	2,79
0,192	2,79
0,198	2,79
0,204	2,79
0,21	2,79
0,216	2,8
0,222	2,81
0,228	2,81
0,234	2,81
0,24	2,81
0,246	2,81
0,252	2,82
0,258	2,83
0,264	2,83
0,27	2,83
0,276	2,83
0,282	2,84
0,288	2,86
0,294	2,86
0,3	2,86
0,306	2,86
0,312	2,86
0,318	2,86
0,324	2,87
0,33	2,88
0,336	2,88
0,342	2,88
0,348	2,88
0,354	2,88
0,36	2,88
0,366	2,9
0,372	2,9
0,378	2,9
0,384	2,9
0,39	2,9
0,396	2,92
0,402	2,92
0,408	2,92
0,414	2,92
0,42	2,92
0,426	2,94
0,432	2,95
0,438	2,95
0,444	2,95
0,45	2,95
0,456	2,95
0,462	2,97
0,468	2,98
0,474	2,98
0,48	2,98
0,486	2,98
0,492	2,98
0,498	3
0,504	3
0,51	3
0,516	3
0,522	3
0,528	3,02
0,534	3,03
0,54	3,03
0,546	3,03
0,552	3,03
0,558	3,05
0,564	3,05
0,57	3,07
0,576	3,07
0,582	3,07
0,588	3,07
0,594	3,1
0,6	3,1
0,606	3,1
0,612	3,1
0,618	3,1
0,624	3,1
0,63	3,11
0,636	3,12
0,642	3,13
0,648	3,13
0,654	3,13
0,66	3,13
0,666	3,16
0,672	3,17
0,678	3,17
0,684	3,17
0,69	3,19
0,696	3,21

0,702	3,21
0,708	3,21
0,714	3,21
0,72	3,25
0,726	3,25
0,732	3,25
0,738	3,25
0,744	3,25
0,75	3,25
0,756	3,25
0,762	3,29
0,768	3,3
0,774	3,3
0,78	3,3
0,786	3,32
0,792	3,35
0,798	3,35
0,804	3,35
0,81	3,35
0,816	3,35
0,822	3,36
0,828	3,4
0,834	3,4
0,84	3,4
0,846	3,4
0,852	3,4
0,858	3,45
0,864	3,46
0,87	3,46
0,876	3,46
0,882	3,46
0,888	3,53
0,894	3,52
0,9	3,52
0,906	3,52
0,912	3,52
0,918	3,6
0,924	3,6
0,93	3,59
0,936	3,59
0,942	3,59
0,948	3,68
0,954	3,67
0,96	3,67
0,966	3,67
0,972	3,67
0,978	3,67
0,984	3,76
0,99	3,77
0,996	3,77
1,002	3,77
1,008	3,77
1,014	3,79
1,02	3,88
1,026	3,87
1,032	3,87
1,038	3,87
1,044	3,96
1,05	3,97
1,056	3,97
1,062	3,97
1,068	3,97
1,074	3,97
1,08	4,07
1,086	4,1
1,092	4,09
1,098	4,09
1,104	4,09
1,11	4,22
1,116	4,22
1,122	4,22
1,128	4,22
1,134	4,21
1,14	4,35
1,146	4,34
1,152	4,34
1,158	4,34
1,164	4,34
1,17	4,49
1,176	4,48
1,182	4,48
1,188	4,47
1,194	4,47
1,2	4,47
1,206	4,63
1,212	4,62
1,218	4,62
1,224	4,62
1,23	4,62
1,236	4,77
1,242	4,78
1,248	4,77
1,254	4,77
1,26	4,91
1,266	4,93
1,272	4,94
1,278	4,94
1,284	4,97
1,29	5,12
1,296	5,12
1,302	5,11
1,308	5,11
1,314	5,11
1,32	5,34
1,326	5,32
1,332	5,29
1,338	5,29
1,344	5,28
1,35	5,51
1,356	5,48
1,362	5,48
1,368	5,47
1,374	5,47
1,38	5,47
1,386	5,68
1,392	5,68
1,398	5,68
1,404	5,78
1,41	5,89
1,416	5,85
1,422	5,85
1,428	5,84
1,434	6,09
1,44	6,05
1,446	6,04
1,452	6,03
1,458	6,03
1,464	6,3
1,47	6,3
1,476	6,27
1,482	6,27
1,488	6,25
1,494	6,51
1,5	6,52
1,506	6,51
1,512	6,93
1,518	6,8
1,524	6,75

1,53	6,73
1,536	6,71
1,542	7,04
1,548	7,05
1,554	7,05
1,56	7,04
1,566	7,39
1,572	7,4
1,578	7,39
1,584	7,39
1,59	7,7
1,596	7,72
1,602	7,71
1,608	7,7
1,614	8,48
1,62	8,55
1,626	8,69
1,632	8,6
1,638	8,7
1,644	8,81
1,65	8,86
1,656	8,89
1,662	8,89
1,668	8,94
1,674	9
1,68	9,03
1,686	9,07
1,692	9,1
1,698	9,11
1,704	9,18
1,71	9,18
1,716	9,24
1,722	9,26
1,728	9,29
1,734	9,33
1,74	9,34
1,746	9,35
1,752	9,4
1,758	9,45
1,764	9,44

1,77	9,47
1,776	9,5
1,782	9,56
1,788	9,56
1,794	9,59
1,8	9,63
1,806	9,6
1,812	9,61
1,818	9,64
1,824	9,64
1,83	9,68
1,836	9,7
1,842	9,71
1,848	9,76
1,854	9,79
1,86	9,75
1,866	9,78
1,872	9,81
1,878	9,83
1,884	9,85
1,89	9,87
1,896	9,86
1,902	9,9
1,908	9,93
1,914	9,92
1,92	9,95
1,926	9,97
1,932	9,98
1,938	9,98
1,944	10
1,95	10,01
1,956	10,01
1,962	10,01
1,968	10,02
1,974	10,03
1,98	10,05
1,986	10,12
1,992	10,1
1,998	10,12
2,004	10,14

2,01	10,16
2,016	10,18
2,022	10,21
2,028	10,19
2,034	10,19
2,04	10,21
2,046	10,21
2,052	10,24
2,058	10,26
2,064	10,26
2,07	10,29
2,076	10,27
2,082	10,28
2,088	10,3
2,094	10,34
2,1	10,34
2,106	10,36
2,112	10,38
2,118	10,39
2,124	10,38
2,13	10,38
2,136	10,39
2,142	10,4
2,148	10,41
2,154	10,41
2,16	10,42
2,166	10,42
2,172	10,45
2,178	10,44
2,184	10,47
2,19	10,47
2,196	10,48
2,202	10,49
2,208	10,49
2,214	10,5
2,22	10,5
2,226	10,53
2,232	10,53
2,238	10,54

Watergroep fulvic acids

Added 0,1 M HCl (mL)	**pH**	**Total volume (mL)**
0	3,17	50
1	2,58	51

Addition of HCl to lower starting pH below 2,7. Titration with NaOH below

Added 0,1 M NaOH (mL)	**pH**
0	2,58
0,006	2,58
0,012	2,58
0,018	2,58
0,024	2,58
0,03	2,58
0,036	2,58
0,042	2,58
0,048	2,58
0,054	2,61
0,06	2,59
0,066	2,59
0,072	2,59
0,078	2,59
0,084	2,6
0,09	2,6
0,096	2,6
0,102	2,61
0,108	2,61
0,114	2,61
0,12	2,61
0,126	2,62
0,132	2,61
0,138	2,61
0,144	2,61
0,15	2,63
0,156	2,62
0,162	2,62
0,168	2,63
0,174	2,63
0,18	2,63
0,186	2,63
0,192	2,64
0,198	2,64
0,204	2,64
0,21	2,64
0,216	2,65
0,222	2,65
0,228	2,65
0,234	2,66
0,24	2,66
0,246	2,66
0,252	2,66
0,258	2,66
0,264	2,66
0,27	2,67
0,276	2,67
0,282	2,67
0,288	2,67
0,294	2,67
0,3	2,69
0,306	2,68
0,312	2,69
0,318	2,69
0,324	2,69
0,33	2,69
0,336	2,69
0,342	2,7
0,348	2,7
0,354	2,7
0,36	2,7
0,366	2,72
0,372	2,71
0,378	2,71
0,384	2,72
0,39	2,72
0,396	2,72
0,402	2,72
0,408	2,72
0,414	2,73
0,42	2,74
0,426	2,74
0,432	2,74
0,438	2,74
0,444	2,75
0,45	2,75
0,456	2,75
0,462	2,76
0,468	2,76
0,474	2,76
0,48	2,76
0,486	2,76
0,492	2,76
0,498	2,76
0,504	2,77
0,51	2,77
0,516	2,79
0,522	2,79
0,528	2,79
0,534	2,79
0,54	2,79
0,546	2,79
0,552	2,82
0,558	2,81
0,564	2,81
0,57	2,81
0,576	2,83
0,582	2,84
0,588	2,83
0,594	2,82
0,6	2,83
0,606	2,83
0,612	2,83
0,618	2,85
0,624	2,84
0,63	2,84
0,636	2,86
0,642	2,87
0,648	2,87
0,654	2,89
0,66	2,87
0,666	2,88
0,672	2,88
0,678	2,89
0,684	2,89
0,69	2,89
0,696	2,9

0,702	2,91
0,708	2,91
0,714	2,91
0,72	2,91
0,726	2,92
0,732	2,92
0,738	2,93
0,744	2,93
0,75	2,93
0,756	2,94
0,762	2,94
0,768	2,95
0,774	2,96
0,78	2,96
0,786	2,97
0,792	2,97
0,798	2,97
0,804	2,98
0,81	2,98
0,816	2,98
0,822	2,99
0,828	3
0,834	3
0,84	3
0,846	3,02
0,852	3,03
0,858	3,04
0,864	3,03
0,87	3,04
0,876	3,05
0,882	3,06
0,888	3,06
0,894	3,07
0,9	3,07
0,906	3,07
0,912	3,08
0,918	3,08
0,924	3,08
0,93	3,09
0,936	3,09
0,942	3,1
0,948	3,12
0,954	3,12
0,96	3,13
0,966	3,13
0,972	3,14

0,978	3,15
0,984	3,15
0,99	3,15
0,996	3,16
1,002	3,17
1,008	3,18
1,014	3,18
1,02	3,19
1,026	3,2
1,032	3,2
1,038	3,21
1,044	3,21
1,05	3,23
1,056	3,24
1,062	3,25
1,068	3,25
1,074	3,26
1,08	3,25
1,086	3,27
1,092	3,28
1,098	3,29
1,104	3,29
1,11	3,32
1,116	3,32
1,122	3,32
1,128	3,33
1,134	3,33
1,14	3,35
1,146	3,37
1,152	3,37
1,158	3,38
1,164	3,39
1,17	3,39
1,176	3,41
1,182	3,42
1,188	3,42
1,194	3,45
1,2	3,46
1,206	3,46
1,212	3,46
1,218	3,48
1,224	3,49
1,23	3,49
1,236	3,5
1,242	3,52
1,248	3,54

1,254	3,55
1,26	3,55
1,266	3,57
1,272	3,6
1,278	3,6
1,284	3,61
1,29	3,62
1,296	3,64
1,302	3,65
1,308	3,66
1,314	3,68
1,32	3,71
1,326	3,7
1,332	3,72
1,338	3,74
1,344	3,75
1,35	3,77
1,356	3,79
1,362	3,8
1,368	3,83
1,374	3,84
1,38	3,85
1,386	3,88
1,392	3,89
1,398	3,93
1,404	3,93
1,41	3,94
1,416	3,96
1,422	4
1,428	4,01
1,434	4,03
1,44	4,05
1,446	4,07
1,452	4,09
1,458	4,11
1,464	4,14
1,47	4,16
1,476	4,19
1,482	4,22
1,488	4,24
1,494	4,26
1,5	4,28
1,506	4,3
1,512	4,33
1,518	4,35
1,524	4,38

1,53	4,41
1,536	4,44
1,542	4,46
1,548	4,49
1,554	4,52
1,56	4,57
1,566	4,58
1,572	4,61
1,578	4,63
1,584	4,67
1,59	4,7
1,596	4,74
1,602	4,76
1,608	4,79
1,614	4,84
1,62	4,88
1,626	4,91
1,632	4,94
1,638	4,98
1,644	5,02
1,65	5,07
1,656	5,12
1,662	5,16
1,668	5,21
1,674	5,23
1,68	5,26
1,686	5,32
1,692	5,36
1,698	5,42
1,704	5,46
1,71	5,51
1,716	5,57
1,722	5,6
1,728	5,68
1,734	5,75
1,74	5,81
1,746	5,86
1,752	5,94
1,758	6,02
1,764	6,1
1,77	6,16
1,776	6,23
1,782	6,32
1,788	6,44
1,794	6,52
1,8	6,64

1,806	6,75
1,812	6,84
1,818	6,97
1,824	7,18
1,83	7,22
1,836	7,37
1,842	7,49
1,848	7,62
1,854	7,76
1,86	7,87
1,866	7,98
1,872	8,13
1,878	8,24
1,884	8,33
1,89	8,44
1,896	8,52
1,902	8,63
1,908	8,69
1,914	8,76
1,92	8,82
1,926	8,84
1,932	8,91
1,938	8,97
1,944	9
1,95	9,06
1,956	9,1
1,962	9,15
1,968	9,19
1,974	9,21
1,98	9,26
1,986	9,29
1,992	9,33
1,998	9,36
2,004	9,39
2,01	9,43
2,016	9,44
2,022	9,47
2,028	9,51
2,034	9,54
2,04	9,57
2,046	9,6
2,052	9,62
2,058	9,63
2,064	9,67
2,07	9,7
2,076	9,73

2,082	9,74
2,088	9,76
2,094	9,78
2,1	9,81
2,106	9,83
2,112	9,84
2,118	9,86
2,124	9,88
2,13	9,91
2,136	9,93
2,142	9,94
2,148	9,96
2,154	9,98
2,16	10,01
2,166	10,01
2,172	10,04
2,178	10,06
2,184	10,06
2,19	10,08
2,196	10,09
2,202	10,11
2,208	10,13
2,214	10,15
2,22	10,16
2,226	10,17
2,232	10,18
2,238	10,19
2,244	10,21
2,25	10,23
2,256	10,24
2,262	10,24
2,268	10,27
2,274	10,28
2,28	10,28
2,286	10,31
2,292	10,3
2,298	10,32
2,304	10,33
2,31	10,34
2,316	10,33
2,322	10,35
2,328	10,36
2,334	10,39
2,34	10,39
2,346	10,4
2,352	10,41

2,358	10,43
2,364	10,43
2,37	10,44
2,376	10,45
2,382	10,45
2,388	10,45
2,394	10,46
2,4	10,49
2,406	10,49
2,412	10,5
2,418	10,51
2,424	10,51
2,43	10,52
2,436	10,53
2,442	10,54

Jadis additive fulvic acids

Added 0,1 M HCl (mL)	pH	Total volume (mL)
0	5,52	50
2	2,51	52

Addition of HCl to lower starting pH below 2,7. Titration with NaOH below

Added 0,1 M NaOH (mL)	pH
0	2,51
0,006	2,51
0,012	2,51
0,018	2,51
0,024	2,51
0,03	2,51
0,036	2,51
0,042	2,51
0,048	2,51
0,054	2,51
0,06	2,51
0,066	2,51
0,072	2,51
0,078	2,51
0,084	2,51
0,09	2,51
0,096	2,52
0,102	2,52
0,108	2,52
0,114	2,52
0,12	2,52
0,126	2,52
0,132	2,52
0,138	2,52
0,144	2,53
0,15	2,53
0,156	2,53
0,162	2,53
0,168	2,53
0,174	2,53
0,18	2,53
0,186	2,54
0,192	2,54
0,198	2,54
0,204	2,54
0,21	2,54
0,216	2,54
0,222	2,54
0,228	2,54
0,234	2,55
0,24	2,55
0,246	2,55
0,252	2,55
0,258	2,55
0,264	2,55
0,27	2,55
0,276	2,55
0,282	2,56
0,288	2,56
0,294	2,56
0,3	2,56
0,306	2,56
0,312	2,56
0,318	2,56
0,324	2,56
0,33	2,58
0,336	2,58
0,342	2,58
0,348	2,57
0,354	2,57
0,36	2,57
0,366	2,57
0,372	2,57
0,378	2,58
0,384	2,59
0,39	2,59
0,396	2,59
0,402	2,59
0,408	2,58
0,414	2,58
0,42	2,58
0,426	2,59
0,432	2,6
0,438	2,6
0,444	2,6
0,45	2,6
0,456	2,6
0,462	2,6
0,468	2,61
0,474	2,61
0,48	2,61
0,486	2,61
0,492	2,61
0,498	2,61
0,504	2,61
0,51	2,62
0,516	2,62
0,522	2,62
0,528	2,62
0,534	2,63
0,54	2,63
0,546	2,63
0,552	2,63
0,558	2,63
0,564	2,63
0,57	2,63
0,576	2,63
0,582	2,63
0,588	2,64
0,594	2,64
0,6	2,64
0,606	2,64
0,612	2,64
0,618	2,65
0,624	2,65
0,63	2,65
0,636	2,66
0,642	2,66
0,648	2,66
0,654	2,66
0,66	2,66
0,666	2,66
0,672	2,66
0,678	2,66

0,684	2,66
0,69	2,67
0,696	2,67
0,702	2,67
0,708	2,67
0,714	2,67
0,72	2,67
0,726	2,67
0,732	2,67
0,738	2,68
0,744	2,69
0,75	2,69
0,756	2,69
0,762	2,69
0,768	2,69
0,774	2,68
0,78	2,68
0,786	2,7
0,792	2,7
0,798	2,7
0,804	2,7
0,81	2,7
0,816	2,7
0,822	2,7
0,828	2,7
0,834	2,71
0,84	2,72
0,846	2,72
0,852	2,72
0,858	2,72
0,864	2,72
0,87	2,72
0,876	2,74
0,882	2,74
0,888	2,74
0,894	2,74
0,9	2,74
0,906	2,74
0,912	2,74
0,918	2,74
0,924	2,76
0,93	2,76
0,936	2,76
0,942	2,76
0,948	2,76
0,954	2,76

0,96	2,76
0,966	2,76
0,972	2,78
0,978	2,78
0,984	2,78
0,99	2,78
0,996	2,78
1,002	2,78
1,008	2,78
1,014	2,78
1,02	2,8
1,026	2,8
1,032	2,8
1,038	2,8
1,044	2,8
1,05	2,8
1,056	2,8
1,062	2,8
1,068	2,82
1,074	2,83
1,08	2,83
1,086	2,83
1,092	2,83
1,098	2,83
1,104	2,83
1,11	2,83
1,116	2,83
1,122	2,85
1,128	2,86
1,134	2,86
1,14	2,86
1,146	2,86
1,152	2,86
1,158	2,85
1,164	2,86
1,17	2,87
1,176	2,88
1,182	2,88
1,188	2,9
1,194	2,9
1,2	2,9
1,206	2,9
1,212	2,92
1,218	2,92
1,224	2,92
1,23	2,92

1,236	2,92
1,242	2,91
1,248	2,92
1,254	2,91
1,26	2,94
1,266	2,95
1,272	2,95
1,278	2,95
1,284	2,95
1,29	2,95
1,296	2,97
1,302	2,97
1,308	2,97
1,314	2,99
1,32	2,99
1,326	2,99
1,332	2,99
1,338	2,99
1,344	2,99
1,35	2,99
1,356	3
1,362	3
1,368	3,02
1,374	3,03
1,38	3,03
1,386	3,03
1,392	3,03
1,398	3,04
1,404	3,04
1,41	3,04
1,416	3,06
1,422	3,07
1,428	3,07
1,434	3,08
1,44	3,07
1,446	3,09
1,452	3,1
1,458	3,11
1,464	3,12
1,47	3,12
1,476	3,13
1,482	3,13
1,488	3,13
1,494	3,13
1,5	3,13
1,506	3,15

1,512	3,15
1,518	3,16
1,524	3,17
1,53	3,19
1,536	3,19
1,542	3,19
1,548	3,19
1,554	3,19
1,56	3,21
1,566	3,22
1,572	3,24
1,578	3,25
1,584	3,26
1,59	3,26
1,596	3,26
1,602	3,27
1,608	3,28
1,614	3,28
1,62	3,29
1,626	3,3
1,632	3,31
1,638	3,32
1,644	3,33
1,65	3,33
1,656	3,34
1,662	3,35
1,668	3,37
1,674	3,38
1,68	3,39
1,686	3,41
1,692	3,42
1,698	3,42
1,704	3,42
1,71	3,43
1,716	3,44
1,722	3,46
1,728	3,47
1,734	3,49
1,74	3,5
1,746	3,51
1,752	3,52
1,758	3,52
1,764	3,53
1,77	3,54
1,776	3,56
1,782	3,57
1,788	3,59
1,794	3,61
1,8	3,63
1,806	3,63
1,812	3,64
1,818	3,65
1,824	3,66
1,83	3,67
1,836	3,68
1,842	3,7
1,848	3,72
1,854	3,73
1,86	3,75
1,866	3,77
1,872	3,77
1,878	3,78
1,884	3,8
1,89	3,82
1,896	3,85
1,902	3,87
1,908	3,9
1,914	3,92
1,92	3,92
1,926	3,93
1,932	3,94
1,938	3,96
1,944	3,97
1,95	3,98
1,956	3,99
1,962	4
1,968	4,1
1,974	4,12
1,98	4,14
1,986	4,16
1,992	4,18
1,998	4,2
2,004	4,21
2,01	4,23
2,016	4,25
2,022	4,28
2,028	4,3
2,034	4,31
2,04	4,33
2,046	4,37
2,052	4,41
2,058	4,43
2,064	4,47
2,07	4,5
2,076	4,52
2,082	4,55
2,088	4,58
2,094	4,61
2,1	4,62
2,106	4,64
2,112	4,67
2,118	4,69
2,124	4,71
2,13	4,74
2,136	4,77
2,142	4,79
2,148	4,78
2,154	4,78
2,16	4,78
2,166	4,78
2,172	4,78
2,178	4,78
2,184	4,78
2,19	4,78
2,196	5,07
2,202	5,06
2,208	5,06
2,214	5,05
2,22	5,05
2,226	5,05
2,232	5,05
2,238	5,05
2,244	5,05
2,25	5,41
2,256	5,39
2,262	5,39
2,268	5,39
2,274	5,39
2,28	5,39
2,286	5,38
2,292	5,39
2,298	5,38
2,304	5,38
2,31	5,78
2,316	5,77
2,322	5,77
2,328	5,76
2,334	5,76

2,34	5,75
2,346	5,75
2,352	5,75
2,358	5,75
2,364	6,24
2,37	6,21
2,376	6,17
2,382	6,16
2,388	6,16
2,394	6,16
2,4	6,15
2,406	6,15
2,412	7,08
2,418	6,91
2,424	6,82
2,43	6,8
2,436	6,78
2,442	6,77
2,448	6,75
2,454	6,75
2,46	6,75
2,466	6,75
2,472	7,83
2,478	7,85
2,484	7,83
2,49	7,81
2,496	7,81
2,502	7,78
2,508	7,77
2,514	7,76
2,52	8,6
2,526	8,7
2,532	8,67
2,538	8,67
2,544	8,66
2,55	8,66
2,556	8,66
2,562	8,65
2,568	8,65
2,574	9,07
2,58	9,06
2,586	9,06
2,592	9,06
2,598	9,06
2,604	9,06
2,61	9,06
2,616	9,06
2,622	9,06
2,628	9,4
2,634	9,39
2,64	9,39
2,646	9,38
2,652	9,39
2,658	9,39
2,664	9,38
2,67	9,38
2,676	9,38
2,682	9,38
2,688	9,62
2,694	9,62
2,7	9,62
2,706	9,62
2,712	9,61
2,718	9,61
2,724	9,61
2,73	9,61
2,736	9,62
2,742	9,81
2,748	9,81
2,754	9,81
2,76	9,81
2,766	9,81
2,772	9,81
2,778	9,81
2,784	9,81
2,79	9,81
2,796	9,81
2,802	9,94
2,808	9,96
2,814	9,96
2,82	9,96
2,826	9,96
2,832	9,96
2,838	9,96
2,844	9,96
2,85	9,96
2,856	9,96
2,862	10,09
2,868	10,1
2,874	10,1
2,88	10,1
2,886	10,1
2,892	10,1
2,898	10,1
2,904	10,1
2,91	10,1
2,916	10,1
2,922	10,21
2,928	10,21
2,934	10,21
2,94	10,21
2,946	10,21
2,952	10,21
2,958	10,21
2,964	10,21
2,97	10,21
2,976	10,21
2,982	10,31
2,988	10,31
2,994	10,31
3	10,31
3,006	10,31
3,012	10,31
3,018	10,31
3,024	10,31
3,03	10,31
3,036	10,38
3,042	10,38
3,048	10,38
3,054	10,38
3,06	10,38
3,066	10,38
3,072	10,38
3,078	10,38
3,084	10,45
3,09	10,46
3,096	10,45
3,102	10,46
3,108	10,46
3,114	10,46
3,12	10,45
3,126	10,46
3,132	10,45
3,138	10,45
3,144	10,45
3,15	10,51
3,156	10,52

Attachment F: PHREEQC model

In all simulations the wateq4f database is used as this one contains fulvic acids and humic acids.

Definitions

```
SOLUTION_MASTER_SPECIES
Fulvate     Fulvate-    0.0   300. 300.
Fulvate(-1) Fulvate- 0.0 300
Fulvate(-2) Fulvate-2 0.0 300
```

With the lines above the molecular weight of fulvate can be changed and the default charge of -2 changed into -1. The bottom two lines are not necessary if a charge of -2 is chosen.

```
EXCHANGE_MASTER_SPECIES
Z  Z+
Fulvate- Fulvate-2

EXCHANGE_SPECIES
Z+ = Z+
log_k 0.0

Cl- + Z+ = ClZ
log_k  0.0
```

The section here is meant to define resin, which is simplified as a fictional molecule Z^+. The log K of counteranion chloride with resin is 0 so any chloride can freely come off the resin when a target anion is present. This is done for simplification reasons so the selectivity of ions can only be changed with log K as done in the next section.

Equations

```
SO4-2 + 2Z+ = SO4Z2
log_k -1.611
-gamma  5.0     -0.040

Fulvate- + Z+ = FulvateZ
log_k -0.93
```

Input

```
SOLUTION 1 # initial solution composition
units mg/kgw
temp  20.0
Resin       0 # virtual species added to define the resin concentration,
only for plotting purposes
pH          8
Cl          0.469   as Cl
S(6)        53.75 as SO4
Fulvate     50 as Fulvate
END
```

The input is defining the chosen water matrix for each solution.

Simulation

```
USE solution 1
EXCHANGE 1
```

```
ClZ 0.000625 # 0.5 g/L resin
SAVE solution 1
END
```

In simulation the water matrix gets to react with the resin. The resin concentration is given in the amount of exchange spots, which is 0.00125 eq/g.

Plotting

Finally the results are plotted. A notepad file with experimental results is co-plotted for comparison purposes.

Attachment G: NOM isolation through dialysis

Materials:

- Membrane tubes (500 D and 1000 D)
- Large jars (3.5 to 5 L)
- Clothespins
- Conductivity meter
- Magnetic stirrer
- Brine
- Demi water

Method:

The large jars are completely filled with demi water. The membranes, filled with brine are then hung inside the jars in a U-shape to have as much osmosis surface as possible to speed up the process. The clothespins are used to attach the membranes to the jars, while also preventing brine to flow out of the tube. The jars are placed on magnetic stirrers to increase the diffusion of ions in the membrane into the demi water. Every 2 hours the conductivity of the demi water is measured to monitor if enough osmosis occurs and the demi water is refreshed. This is repeated until the conductivity of the demi water at refresh times has barely increased, signifying that most ions have been removed from the brine.

Attachment H : Alternative method for calculating organic charge

Sum $[Org^-] = [H^+] + [Na^+] – [OH^-] – [Cl^-]$

Since all other ion concentrations can be calculated the organic charge can be calculated as well. Chloride comes from the background electrolyte and the HCl to initially reduce pH. Sodium comes from the background electrolyte and the titrant. H^+ and OH^- can directly be determined from the pH.

$[H^+]$ = 10^(- pH)
$[OH^–]$ = 10^(-14 + pH)

These two values are corrected with an activity coefficient. This value is dependent on the ionic strength. Since this ionic strength is in return dependent on the concentrations, this becomes an iterative process:

I = 0.5*Sum(c.z^2)

Where

z = ionic charge
c = concentration

I = 0.5*(Sum $[Org^-] + [H^+] + [Na^+] + [OH^-] + [Cl^-]$)

Due to the background electrolyte of 0.1 M NaCl it is assumed that other ions have relatively negligible effect on I and I is therefore assumed as 0.1.

The activity coefficient (y) is then determined with Debye-Hückel

Log (y) = -0.5085*z^2*Sqrt (I)

With I = 0.1 and z=1 this gives

Y = 0.6906

This gives final corrected values

$[H^+]$* = 0.6906*10^(- pH)
$[OH^–]$* = 0.6906*10^(-14 + pH)

While this method is succesfully used in other NOM titrations (J.Ritchie, 2002) this method for calculating NOM charge gave remarkable results in titrations done in this research and are therefore not used. As can be seen in the figure below the curve is similar to the method with subtracting a blanc for the largest part but does not flatten out towards the end.

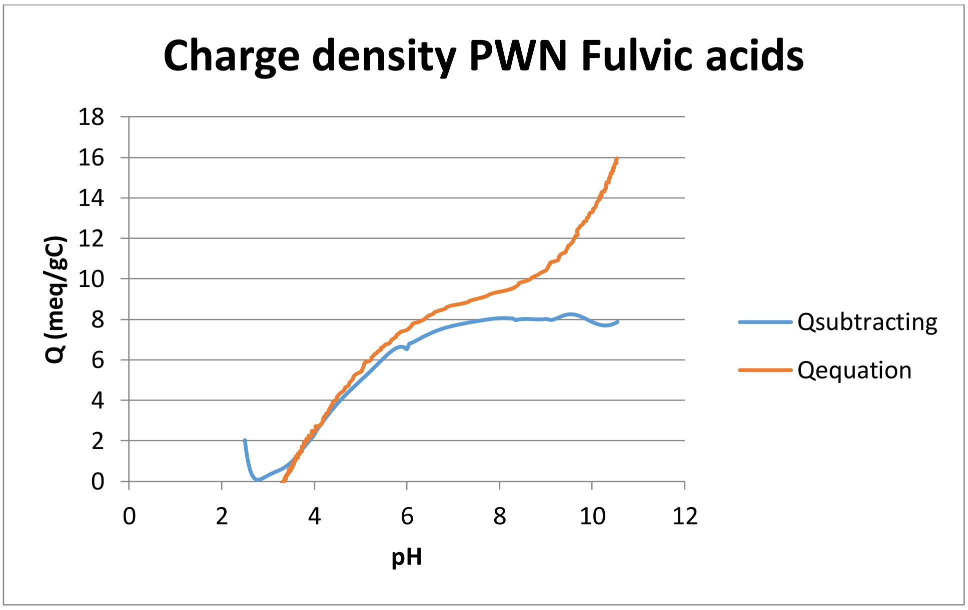

Figure 45: Charge density PWN fulvics, comparison of 2 methods of determining organic charge

Attachment I: Carbonate equilibrium

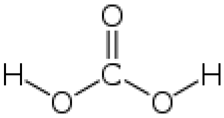

Figure 46: Carbonic acid structure formula

The carbonate equilibrium is based on the carbonic acid's (H_2CO_3) behavior in water. Carbonic acid is both a carboxylic acid and a polyprotic acid, meaning it has two protons that it can donate when the pH increases. This will leave either bicarbonate (HCO_3^-) or carbonate ($CO3^{2-}$) through the following reactions, based on the pH:

$H_2CO_3 <> H^+ + HCO_3^-$
$HCO_3^- <> H^+ + CO3^{2-}$

Carbonic acid is not very stable and by lowering the pH, the chemical equilibrium will shift to form carbon dioxide (g) which will get stripped from the solution into the atmosphere:

$H_2CO_3 <> H_2O + CO_2$

All above mentioned equations are active simultaneously, leading to a complex system of similar molecules that is dependent on the pH of the water. The graph below shows which fractions are present for a certain pH. When the pH goes below 6 the majority of carbonic acid has turned into carbon dioxide and will get stripped if the water is in contact with the atmosphere. At neutral pH the main component is bicarbonate. At a pH of around 10 or higher most of the bicarbonate will change to carbonate.

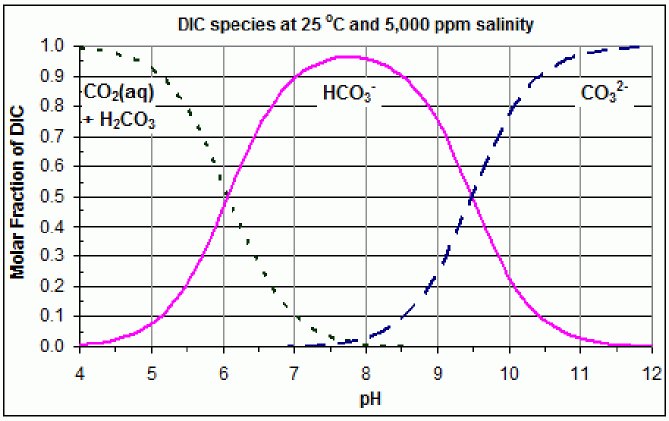

Figure 47: Carbonate equilibrium

Since bicarbonate and carbonate are negatively charged these molecules will adsorb to anion resins and compete for available exchange spots with other anions. This adsorption and the carbonate equilibrium occur simultaneously and both influence bicarbonate levels in the water. Therefore, it is important to know the pH to get an indication of the amount of (bi)carbonate present in the water.

Measuring (bi)carbonate

Measuring bicarbonate and carbonate has shown to be a difficult process for various reasons. The risk for errors is high as the concentrations fluctuate and are influenced by the atmosphere and other ongoing pH changing reactions. There is not a simplified method such as a test kit available for bicarbonate. Experiments has to be performed under controlled airtight conditions. These reasons make determination of bicarbonate not easily accessible and a program as PHREEQC that could provide a first estimate will be a good alternative.