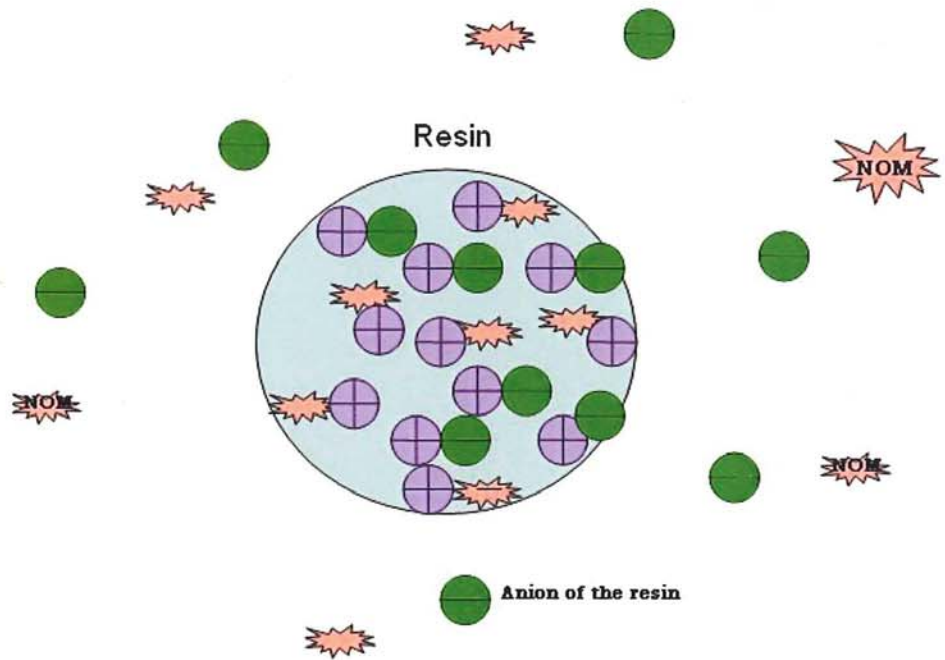


Ion exchange for NOM removal in drinking water treatment

February 2008

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waternet

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Ion exchange for NOM removal in drinking water treatment

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Abstract

Ion exchange resins have found an increasing application in the drinking water treatment sector over the last few decades. The ion exchange resins have a positive ability to remove the charged natural organic matter (NOM). To apply this process in full-scale treatment, the most suitable resin has to be selected and the hydraulic behaviour of the treatment process must be known.

This study has the purpose to study the NOM fractions removal with different resins and select the most suitable resin for NOM removal of the Weesperkarspel water. Another purpose is to study the hydraulic behaviours of fluidized ion exchange and testing of the fluidization models of Ergun and Richardson-Zaki.

The thesis study is characterizing NOM into the specific fraction and later observing the removal of each fraction with the different ion exchange resins. The kinetic and the equilibrium of NOM removal of each resin are also studied. Four ion exchange resins are tested (Lewatit VP OC 1071, Purolite Macronet 200, Duolite A7 and MIEX DOC). The ultraviolet absorbance method (UV), dissolved organic carbon detection method (DOC), specific ultraviolet absorbance (SUVA), fluorescence excitation emission matrix (fluorescence EEM) and liquid chromatography-organic carbon detector method (LC-OCD) were applied.

Weesperkarspel water contains a high degree of aromatic NOM fractions, mostly in the form of humic substances. The Lewatit VP OC 1071 is the most suitable resin for removal of NOM in general view, especially aromatic NOM and humic substances fractions. It appears to be removed as high as 65% and 94% respectively. The MIEX DOC removed 57% aromatic NOM fraction and 70% of humic substances. The pH was found as the dominant parameter for the NOM removal by the weak base Duolite A7. In normal raw water (pH = 7.8), this resin is almost ineffective while it can remove the aromatic NOM up to 35% and humic substances fraction of 45% in raw water pH adjusted to 5. The sorbent Purolite Macronet 200 can remove only biopolymers and neutral NOM fractions. Adsorption is an important mechanism for the removal process of high molecular weight NOM fractions and the neutrals fractions.

By using the linear driving force model (LDF) to describe the ion exchange rate of the resin, it was found that MIEX DOC resin can remove NOM faster than other resins. The LDF- k constant of MIEX DOC is also higher than other resins. MIEX DOC has the smallest resin bead size. This can be the reason for the fast removal of NOM. The resin exchange capacity is related with the Freundlich constant K and n . Increase of K and n values lead to increase of exchange capacity. The Lewatit VP OC 1071 has the highest K and n values and thus the highest exchange capacity.

The exchange rate and exchange capacity is a specific property of each resin. With help from the LDF model and Freundlich isotherm the breakthrough curve can be determined. The Lewatit VP OC 1071 has longest running time compared with the MIEX DOC and Duolite A7 due to the highest exchange capacity.

The hydraulics behaviour of fluidized bed ion exchange has been investigated with the strong base gel resin Lewatit VP OC 1071. The temperature and the feed velocity influence the expanded behaviour. The wet density and wet porosity are important parameters for the model prediction.

Combination of mathematical modelling of ion exchange and the treatment conditions of Weesperkarspel drinking water treatment plant, the fluidized ion exchange process can be designed. For Weesperkarspel drinking water treatment plant, the aim is to decrease the DOC concentration of 7.2 mg C/l to 3.0 mg C/l with the fluidized ion exchange process. The 20 fluidized

ion exchange reactors with a height of 9 m, 10 m² of resin bed surface area, a bed height of 2 m and a feed velocity of 20 m/h are designed. The reactors consist of 4 groups, each group is started with delays of 15 days. With this operational step, the running time of each reactor is 60 days. The cost is estimated 11-euro cent per m³ treated water.

Keywords: NOM (characterization), ion exchange resins, ion exchange rate, linear driving force model, Freundlich isotherm, fluidized ion exchange, fluidization model

List of Symbols

C	Concentration of NOM	(mg/l)
C_0	Initial concentration of NOM at time t	(mg/l)
C_t	Concentration of NOM at time t	(mg/l)
C_e	Concentration of NOM at time equilibrium	(mg/l)
C_{wl}	Drag coefficient Ergun	(-)
d_r	Resin effective diameter	(m)
D	Column diameter	(m)
g	Gravitational acceleration	(m/s ²)
Ga	Galileo number	(-)
H	Expanded bed height	(m)
H_0	Initial bed height	(m)
k	Linear driving force constant	(h ⁻¹)
K	Freundlich isotherm constant	(g/kg*(m ³ /g) ⁿ)
L	Bed height	(m)
m	Resin mass	(kg)
n	Freundlich isotherm constant	(-)
n	Empirical parameter of the Richardson-Zaki equation	(-)
p	Expanded resin porosity	(-)
p_0	Resin bed porosity	(-)
ΔP	Pressure drop	(Pa)
Q	Exchange amount of NOM	(mg/l)
Q_e	Exchange amount of NOM at equilibrium	(mg/l)
Re_0	Terminal settling Reynolds number	(-)
Re_h	Particle Reynolds number	(-)
T	Temperature	(°C)
v	Feed velocity	(m/s)
v_0	Terminal velocity	(m/s)
ν	Viscosity of water	(m ² /s)
ρ_r	Resin density	(g/l)
ρ_w	Water density	(g/l)

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1 Introduction

1.1 Background

Several studies pointed out that natural organic matter (NOM) might have a negative effect on treatment processes. They reduce the efficiency of water treatment processes and at the same time increase the investment cost and the operational cost.

NOM is often found in soil and all water resources, especially in surface water, for example in lakes, rivers and reservoirs. NOM contains a variety of compounds that also have a variety in size, chemical composition, structure and functional groups depending on the origin and age of the material, such as humic substances, hydrophobic compounds, hydrophilic compounds, small organic acids, aromatic compounds, proteins and amino acids (Amy *et al.*, 2004; Chen *et al.*, 2003; Kitis *et al.*, 2001). The NOM changes seasonally both quantitatively and qualitatively. In Scandinavia, the trend of NOM concentration is found an increase according to the long-term climate change (Korth *et al.*, 2004).

NOM has now become the global problem in the drinking water treatment industry that every part of the world is facing. NOM may cause colour, odour and taste problems and disinfectant by products (DBP's) formation where NOM is the precursor. The Netherlands, where chlorination process is not used, is facing the problem of bacteria growing in the distribution system. It was also found that the Legionella bacteria have been growing in the warm water installation. The Legionella problem might lead to consumers losing confidence in tap water and turn to the consumption of bottled water.

In treatment processes, NOM can cause fouling in membrane filtration, clogging in granular activated carbon filtration process (GAC) due the large range of NOM molecular sizes and varied in fraction properties. NOM can also cause an increase of the coagulant and ozone dosing in order to increase the removal efficiency and the biodegradation (Korth *et al.*, 2004). The result of the presence of NOM is an increase of operational cost and therefore consequences the increasing of the drinking water price.

In the past, the removal of specific NOM fractions did not receive much attention because it was complicated and expensive. Nowadays, with combination of technologies different fractions of NOM can be determined, which gives more insight in the effects of NOM in the treatment and the distribution system.

The ion exchange process for the removal of NOM receives much attention in drinking water treatment sector in last few decades. The ion exchange is an alternative drinking water treatment process when the main problem is a high concentration of NOM in raw water. The operational costs and the installation costs of ion exchange process are lower compared with the GAC and the operation is simple (Bolto *et al.*, 2004; Heijman *et al.*, 2002). Besides that, the removal efficiency

of NOM with ion exchange process is found at a high percentage especially the humic substances fraction, constitute about 50-80% of total NOM (Bolto *et al.*, 2004).

The application of ion exchange is mostly placed in the form of a fixed bed, but the disadvantage is the risk for rapid bed clogging by suspended solids. The ion exchange resin filter bed has to be back washed frequently. The operational cost is consequently increased and also increasing problems with the waste from the regeneration process occur. Fluidized ion exchange is expected to be a better possibility for the application of ion exchange process. In order to apply fluidized ion exchange, it is necessary to understand the hydraulics of the resin fluidization. Therefore a fluidization model is necessary. In order to predict expanded bed porosity and expanded bed height in relation to operational conditions, such as the ion exchange resin bead size, density, feed velocity and water temperature.

1.2 Problem analysis for Weesperkarspel drinking water treatment plant

The Weesperkarspel (WPK) drinking water treatment plant provides about 31.3 million m³ per year for the city of Amsterdam and surrounding areas. The raw water is collected from the Bethune polder, sometimes mixed with water from the Amsterdam Rhine canal. The raw water is coagulated with ferric chloride (FeCl₃) in a horizontal settling tank in order to remove the suspended solids, phosphate and heavy metals. The quality of the water improves further with sedimentation, biodegradation and auto-purification processes in a reservoir of 130 hectares with retention time of 100 days. With rapid sand filtration the reservoir water is pre-treated, resulting in the removal of ammonium, suspended solids and algae. The pre-treatment is placed in Loenen. The dissolved organic carbon (DOC) concentration, UV₂₅₄ absorbance, water temperature and the pH of the pre-treated water during the year 2004-2005 are shown in Table 1.

Table 1 DOC concentration, UV₂₅₄ absorbance, pH and temperature data of WPK water after pre-treatment during year 2004-2005.

DOC	UV ₂₅₄	pH	Temperature
mg C/l	Ext/m	-	°C
5.3-7.2	12.6-15.5	7.3-7.7	2.3-22

After the pre-treatment process, the water is transported to the WPK drinking water treatment plant. The first process in the post-treatment is ozonation to increase biodegradability of the NOM and for disinfection. Thereafter, pellet softening reactors are used to reduce hardness. The third step is biological granular activated carbon filtration (BAC). It is applied to remove (DOC), assimilable organic carbon (AOC) and the micro-pollutants. The last step in treatment is slow sand filtration for further reduction of suspended solids. This process is also the second barrier against pathogens and especially important to remove persistent pathogens with low susceptibility for ozone such as *Cryptosporidium*. The process scheme of WPK treatment plant is shown in Figure 1 (Bosklopper *et al.*, 2005).

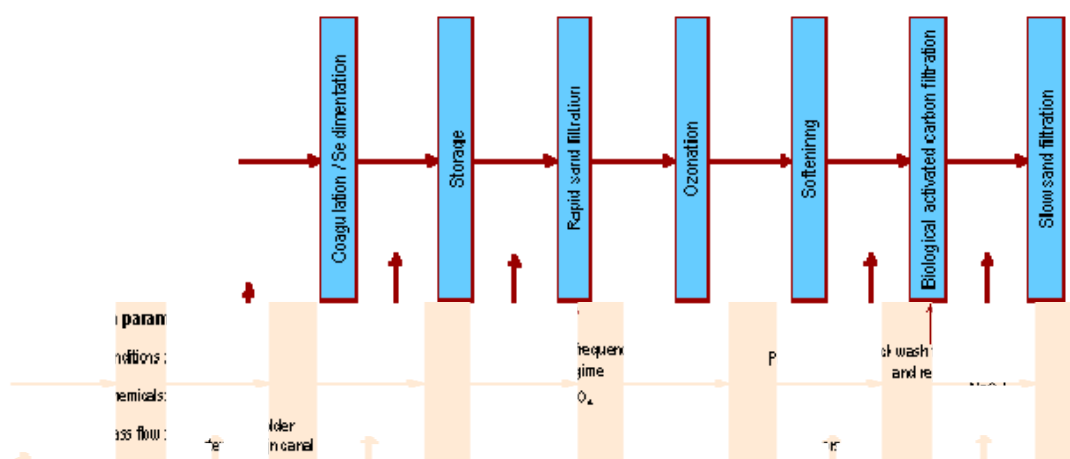


Figure 1 The process scheme and the operation parameters of the WPK drinking water treatment plant.

As can be seen from Figure 1, NOM is mostly removed in BAC process with the help of the ozonation process. High amounts of ozone have to be dosed in order to increase the biodegradability. The NOM also causes clogging problems in BAC process. The BAC has to be regenerated frequently and leads to decrease of pesticides removal efficiency. The operational costs and the removal efficiency of ozonation and the BAC might be better if NOM is first removed. Therefore the drinking water company decided to find the new technology for NOM removal with the assumption that when the NOM is first removed in pre-treatment process before the existing treatment processes, the service time of the existing treatment processes will be longer and the operational cost could be decreased.

This thesis study is part of the research towards the implementation of fluidized ion exchange process in the WPK drinking water treatment plant.

1.3 Objective

Main purpose of the thesis is to study the possibility to implement the fluidized ion exchange process for NOM removal at WPK water treatment plant. The new process for NOM removal is required in order to reach the production aim of high treatment performance and cost effectiveness.

To reach the main purpose of the thesis, the suitable resin needs to be found and tested on fluidization behaviour of the ion exchange resin. Therefore, some sub-objectives are investigated.

1. Study the removal of NOM with different ion exchange resins. This study provides also information about the different NOM fraction removal.
2. Study the kinetics and the equilibrium of each resin to be applied in the breakthrough curve prediction model.
3. Study the hydraulic behaviour of a fluidized ion exchange and to test the fluidization models to design the fluidized ion exchange reactor.

1.4 *Layout of thesis*

Chapter 2 gives a comprehensive review of the literature, the ion exchange theory and mechanism, the ion exchange model for kinetics of NOM removal and equilibrium of NOM removal and the fluidization model used for the fluidized ion exchange behaviour prediction.

Chapter 3 introduces the experiments with ion exchange resins, including materials, methods, analysis method and the experimental set-up.

Chapter 4 presents the results and discussions of the experiments. Characterization of NOM fractions with different analysis methods, the breakthrough curve of each resin and the result of fluidization model prediction compared with measurement data for fluidized ion exchange are presented.

Chapter 5 is the design of the full-scale fluidized ion exchange reactor for WPK water treatment plant. The predicted breakthrough curve of ion exchange process is also presented.

Chapter 6 provides the conclusion of the thesis study and the recommendations for further research on this topic.

2 Literature reviews and theory

2.1 Characterization of natural organic matter

Characterisation of natural organic matter (NOM) is necessary to understand how NOM impacts on the treatment processes and NOM removing process. In this thesis, NOM fractions are characterized with five different methods, described in the following.

2.1.1 Dissolved organic carbon

Dissolved organic carbon (DOC) is a dissolved organic material in water. DOC can be determined with DOC or total organic carbon (TOC) analyser. The methods used is the patented photocatalytic oxidation, that decomposes all organic compounds in the water sample to give carbon dioxide, water and acid, base or salt of any other organically bound elements. The resulting CO₂ gas is accurately determined and converted to concentration of organic carbon in the water. Often, NOM is expressed as DOC because the DOC analysis is not complicated and not costly compared with other methods. The DOC concentration measurement is required in this thesis study for the modelling part. DOC is used as the water quality parameter to determine the ion exchange breakthrough curve.

2.1.2 Ultraviolet absorbance

The ultraviolet absorbance (UV) is a relatively small part of the electromagnetic radiation spectrum and the shorter the wavelength the more penetrating the radiation. The region where a compound absorbs radiation depends on the energy of the molecular transitions. High-energy electronic transitions are observed in the low-wavelength regions. Moderate-energy transitions are observed in the high-wavelength region. For the drinking water sector, UV absorbance at 254 nm is often used as representative of NOM compounds. This wavelength is introduced to represent the NOM concentration because an aromatic or unsaturated organic compound mostly absorbs it, which is frequently the main part of NOM. Another UV wavelength that is commonly used to monitor the aromatic NOM is 280 nm. This wavelength is introduced to represent the aromatic NOM because it is found that many aromatic compounds have shown the electron transition in this UV region (270-280 nm) for instance phenolic acid, benzoic acids, polygene and polycyclic aromatic hydrocarbons (Uyguner *et al.*, 2005).

Uyguner *et al.* (2005) have reported that the organic nitrogen NOM fraction has a high relative absorption at lower wavelength (lower than 240 nm). Moreover this UV absorbance region is normally applied to observe the presence of nitrate ions in the raw water. The UV₂₃₀ could be able to monitor the amount of small organic nitrogen in raw water. In this thesis study UV absorbance of the water sample is applied at 3 UV wavelengths (230 nm, 254 nm and 280 nm) with the assumption that UV₂₃₀ can be a representative of organic nitrogen and UV₂₅₄, UV₂₈₀ absorbance are monitoring to the aromatic NOM fraction.

2.1.3 Specific ultraviolet absorbance

By combining DOC and UV_{254} into one single parameter, the specific ultraviolet absorbance (SUVA) can be calculated (Eq.1). This provides a quantitative measurement of the aromatic content within NOM.

$$SUVA = \frac{UV_{254}}{DOC} \quad \text{Eq.1}$$

The SUVA is applied to fractionate NOM into humic substance when $SUVA > 4$. When SUVA value is about 2 to 4, the water contains a mixture of humic acids and other NOM components. When SUVA is lower than 2, it contains mainly a low molecular weight fraction. SUVA also can indicate the composition of water in terms of hydrophobicity and hydrophilicity. $SUVA > 4$ indicates mainly the hydrophobic and especially the aromatic compound while $SUVA < 2$ represents hydrophilic compounds (Uyguner *et al.*, 2005).

2.1.4 Fluorescence excitation emission matrix spectroscopy

The principle of fluorescence is the capacity of a molecule to absorb light of a certain wavelength and light excitation of another wavelength depending on specific molecular bonds. This method has become popular because of its acute sensitivity to changes in properties of the molecule. Fluorescence can be excited at a wide range of wavelengths and detected over a similar wavelength range. Excitation and emission wavelengths are detected with delays of around one minute (Yan *et al.*, 2000; Royer, 1995).

The absorbance intensity data of emission spectra at multiple excitation wavelengths give information about different NOM fractions. To indicate the NOM fractions, three dimensions or contour pictures are made of fluorescence intensity as a function of excitation and emission wavelength as shown in Figure 2. The occurrence of specific peaks in the picture can provide some information about the composition and source of NOM in the water. With this technique NOM can be divided into 2 main groups which are the humic substances, of which the peak mostly occurs in the high emission wavelength between 410- 480 nm in combination with excitation wavelength between 220-260 nm and 300-370 nm. Another NOM fraction is a proteins-like where the peak occurs at low emission wavelength of 300-350nm and excitation wavelength of 220-280 nm (Herzsprung, *et al.*, 2005; Burdige *et al.*, 2004).

Chen *et al.* (2003) divided the NOM compositions with the same fluorescence excitation emission matrix (fluorescence EEM) method into five fractions. They state that the high molecular weight NOM fraction peak occurs in the region of about 380-480 nm emission wavelength combinations with high excitation wavelength of higher than 250 nm. The majority of this fraction consists of a humic acid-like. At the same emission wavelength combination with a low excitation wavelength of lower than 250 nm, they gave the definition as the fulvic acids-like region. Microbial by-products-like region is located at excitation wavelength higher than 250 nm combined with an emission wavelength lower than 380 nm. Two more regions are aromatic proteins-like regions, both located at low emission and excitation wavelength of lower than 380 nm and 250 nm respectively. The aromatic proteins-like region is divided into two

small regions due to the different in molecular weight and molecular structure. The five fluorescence EEM regions of Chen *et al.* (2003) are shown in Figure 2.

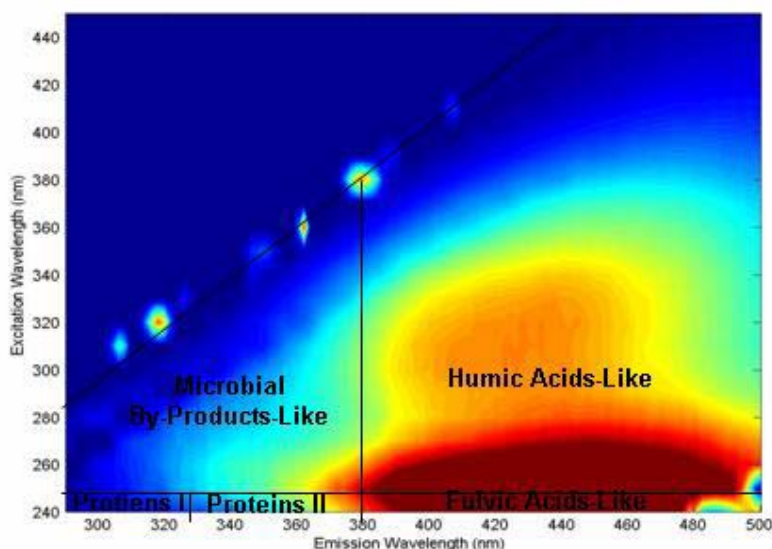


Figure 2 The fluorescence EEM regions of Chen *et al.* (2003).

2.1.5 Liquid chromatography organic carbon detection

Liquid chromatography organic carbon detection (LC-OCD) method uses the difference in speed of diffusion through porous beads in a column. The molecule that is smaller than the pores can diffuse into the pores. Larger molecules are faster restricted to the pore. LC-OCD is in essence a physical sieving process (Huber, 2005). A test chromatogram of LC-OCD method is shown in Figure 3.

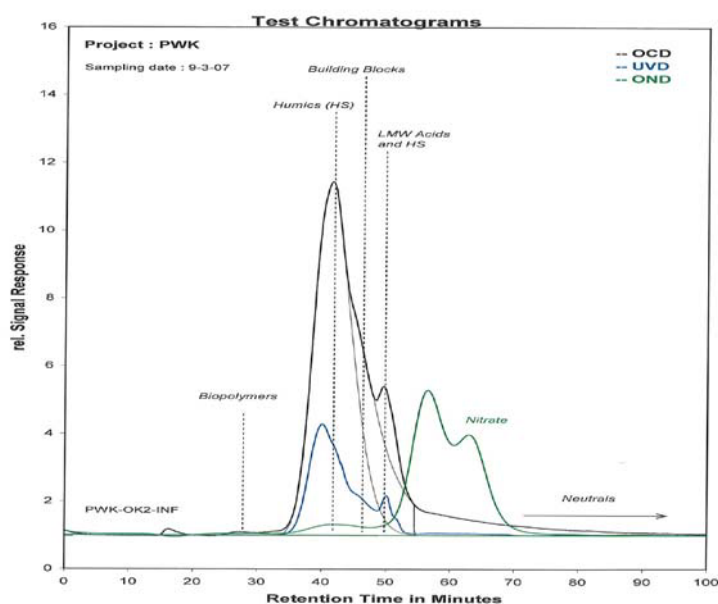


Figure 3 Test chromatogram of raw WPK water resource.

According to the differences in molecular weight of NOM compounds, the LC-OCD method is able to separate NOM compounds into 5 difference groups. (Huber, 2005; Amy, *et al.*, 2004).

- (i) Polysaccharides/proteins or Biopolymer (>20.000 g/mol).
- (ii) Humic substances (1000 g/mol).
- (iii) Building blocks (breakdown products of humic substances, 300-450 g/mol).
- (iv) Low-molecular weight organic acids (<350 g/mol)
- (v) Low-molecular weight neutrals and amphiphilics (<350 g/mol)

2.2 Natural organic matter removal with ion exchange

2.2.1 Resin properties

Gel versus Macroporous resin

Gel ion exchange resins are composed of a polymer matrix, which results in the formation of a homogeneous continuous phase throughout the bead. The pore structure of gel resins depends on the degree of cross-linking that is varying between 2 and 20% divinylbenzene (DVB) in the polymer matrix. The resin swells under some exchange conditions. Due to the ability to swell, the diffusion resistance of compound ions into the resin bead is decreased and hence higher rates of ion exchange can occur. It is noticed that the exchange capacity of a gel resin is usually higher than a macroporous resin (Bolto *et al.*, 1987).

Macroporous resins are not transparent due to the fact that they contain up to 20% DVB in the polymer matrix. They are produced from a styrene-DVB copolymer to which has been added non-polymerizable diluents that volatilizes leaving discrete macro pores throughout the bead. These pores are considerably larger than those found in gel resins and allow the accessibility of large molecules. The macroporous resin has a higher degree of cross-linking, little volume change is exhibited in any solvent (Bolto *et al.*, 1987)

The papers of the NOM removal with different types of resin by Croue *et al.* (1999) [Dowex MSA-1, Dowex 11 and IMAC HP661] and Tan *et al.* (2005) [Dowex Marathon A, Dowex 22 and Dowex M-43] show that the gel resin is the most effective in NOM removal compared with strong base macroporous and weak base macroporous resins. The gel resin mostly has a higher exchange capacity than the macroporous resin except for some special macroporous resins such as MIEX. The structure of gel resin might be an important aspect for the ion exchange process. The gel resin has a light crosslink compared with the high crosslink of the macroporous one. It has a higher degree of swelling. While Bolto *et al.* (2004) and Fetting *et al.* (1999) have found that the macroporous resin is most suited for the removal of NOM. According to the pore structure, NOM can easier access into the resin structure matrix. The experiment results and discussions above were only based on the DOC removal measurement and UV absorption measurement. The exact properties of NOM such as the NOM fraction and the molecular weight were not investigated. As mentioned in the chapter 1 that NOM properties are dependent on the origin, time and place, this reason might leads to opposite of the research conclusion.

Water content

When the dry ion exchange resin is soaked in water, it adsorbs a certain proportion of water. The volume of water that the resin can absorb is defined as the water content or moisture content. Ion exchange resins may also be considered as relatively concentrated electrolytes that try to dilute themselves by adsorbing water under influence of osmotic pressure (Wachinsky, 2006). The water content gives an influence on the NOM removal. Bolto *et al.* (2004) did tests with resins of different water contents varying from 43% to 90%. They found that higher water content resin decreased higher amounts of UV absorbance. When a resin adsorbs more water, the resin particle is more swollen, as a consequence the diffusion resistance for NOM ions is decreased. Thus the NOM ion can easier penetrate into the resin.

Strong base versus weak base resin

The strong base resin is more ionized and can operate over the entire pH range. Therefore, it can remove both highly and weakly dissociated NOM compounds. The strong base resin can be divided into two types. Type I with a quaternary ammonium group and type II with a slightly modified quaternary ammonium group where a methyl group is replaced with an alcohol group. Type I often has less exchange capacity but more stability than type II. The weak base resin often has exchange groups such as a tertiary amino groups or a mixture of two or more amino groups. As an amino group is only weakly basic, it does not dissociate in an alkaline solution. Therefore, it can operate only in salt form with a pH lower than 7. A weak base resin is only suitable for removal of highly dissociated NOM. The exchange capacity of weak base resins is related to the pH value of the influent water. More acidic the pH of water, better the dissociation of the exchange groups and the higher the exchange capacity (Wachinsky, 2006; Bolto *et al.*, 1987).

Several researchers have concluded that the strong base resin performs better than weak base resins in NOM removal (Tan *et al.*, 2005; Bolto *et al.*, 2004; Croue *et al.*, 1999). Most researches have been carried out in the pH range of natural raw water, which is about 6 to 8. With this pH, the weak base resin was not completely ionized. This might be a reason that NOM removal results of weak base resin are less than strong base resin.

The regeneration process is an advantage of weak base resins. The regenerated resin maintains high exchange capacity. The captured ions are easily eluted because of their weak base chemistry (Wachinsky, 2006). The regenerant requires much less concentration and volume than strong base resin. However, Siegers *et al.* (2001) have experimented with the strong base Purolite A-860 and found that this resin can also maintains an exchange capacity of higher than 91% after regeneration with 10% of NaCl solution.

Resin bead size and surface area

The particle size of the resin is a dominant parameter for ion exchange process. In the exchange mechanism a large contact surface is required. As a consequence, the smaller resin bead size is more suitable for NOM removal (Humbert *et al.*, 2005; Bolto *et al.*, 2004). Fearing *et al.* (2004) have experimented with the MIEX, which is a small bead size resin and have concluded that MIEX is more suitable for removing middle and lower molecular weight NOM fractions and less effective for the high molecular weight fraction. Smaller bead size has a less open structure, where only

the middle and the small NOM fractions can pass through. In addition, even though the smaller resin bead size offers an increase in exchange rates, in the operation of the process, it can result in excessive pressure drops, difficult to keep the resin in the bed (for the fluidized bed) and increasing the risk of clogging and fouling problems (for the fixed bed) (Wachinsky, 2006).

2.2.2 Raw water properties

Origin of raw water

Raw water quality depends on time and place. Croue *et al.* (1999) experimented with 2 different water sources with 3 anion exchange resins, and found that the removal efficiency depends on the origin of NOM. The hydrophobic NOM fraction obtained from the first source is easier to remove than the same fraction from the second source. This report shows that within the same NOM fraction different compound structures might exist.

Size and charge density of NOM in raw water

Size and charge density are dependent parameters. Large molecules usually contain a lower charge. The NOM fraction that contains higher charge density is the most preferential to be removed. The ion exchange process is usually not effective in removing neutral hydrophilic compounds (Bolto *et al.*, 2004; Croue *et al.*, 1999). Hongve *et al.* (1999) researched with resin Duolite A 171 and found that organic acids with low molecular weight and a high charge density were first to be adsorbed. The large molecules need more contact time with resin to become adsorbed. Colour is less removed compared with other compounds because it consists of large molecules and less charge density.

Ionic strength of the raw water

The presence of other anions in raw water has influence on the ion exchange process, because some can easier exchange with the chloride ion or hydroxyl ion of the resin than NOM because of their higher charge. For example, sulphate can react more quickly with the chloride ion of the ion exchange resin (Hongve *et al.*, 1999).

2.3 Ion exchange mechanisms

There are two mechanisms involved in ion exchange processes.

- Ion exchange mechanism or electrostatic interaction
- Surface adsorption mechanism

The ion exchange mechanism is known as the dominant mechanism for the process while the surface adsorption mechanism is mostly neglected. However, some researchers reported that surface adsorption is involved in the ion exchange process for the neutrals and the smaller NOM fractions (Fettig, 1999).

The ion exchange process is a reversible interaction of ions between a solid phase (the ion-exchanger/resin) and a liquid phase (NOM in water)

The ion exchange mechanism can be presented as Eq. 2 and Figure 4.



Where R is the cation site on the resin, A is the anion site on the resin surface, B is the anion in the water.

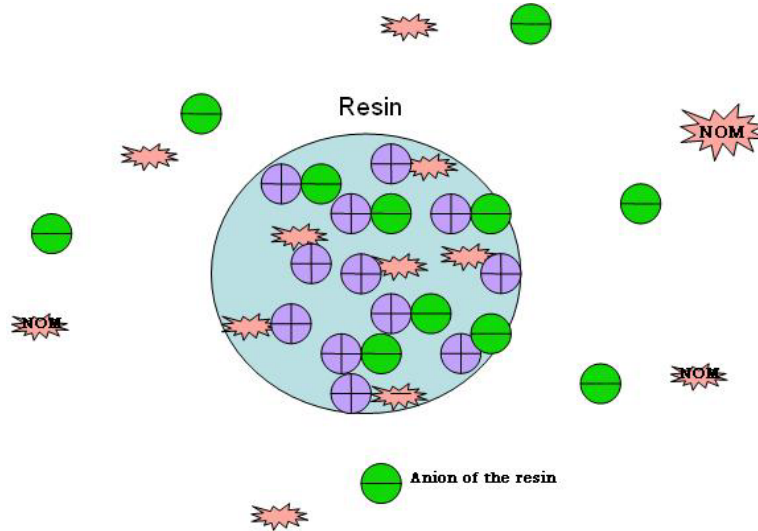


Figure 4 The ion exchange process.

The reaction equation 2 consists of two processes that are:

1. The exchange process; this process is a normal operation where NOM ion is exchanged with anion on the resin surface.
2. The regeneration process; this process occurs whenever the chloride or hydroxyl concentration is rich in water; the resin will take the chloride ion into its surface and release the NOM ion into the water.

2.4 Mathematical modelling of ion exchange

Assumed is that the ions, which the resin releases during the exchange process, have no influence on the exchange process. And the resin properties are not changed. The ion exchange process can be described with the following principles.

In order to describe the exchange term, the linear driving force model (LDF) is applied. This model provides the relationship between the ion exchange rate, the ion exchange isotherm and the LDF- k kinetic constant.

$$\frac{\partial Q}{\partial t} = k(Q_e - Q) \quad \text{Eq. 3}$$

The LDF- k constant can be measured in batch experiment by transforming Eq. 3 into an exponential form Eq. 4.

$$C_t = (C_0 - C_e)e^{kt} + C_e \quad \text{Eq. 4}$$

For the equilibrium of the ion exchange process, the Freundlich isotherm is applied. Freundlich concluded empirically that the following holds for most systems at the equilibrium as shown in the Eq. 5.

$$Q_e = KC_e^n \quad \text{Eq.5}$$

This empirical equation is usually applied to describe the adsorption process where the solid particle is used to remove a soluble substance from water. With this adsorption condition and the assumptions above, this equation can also be applied for the ion exchange.

With Eq.3-5 and batch experiment, it is possible to determine the LDF- k constant and the Freundlich constants. They can be used to predict the full-scale operation of the ion exchange process and the ion exchange breakthrough. To solve Eq.3-5, the Stimela model is applied.

Stimela model

Stimela is an environment for standardised mathematical models of drinking water treatment processes. Stimela is developed by DHV and Delft University of Technology and is especially designed for water quality modelling. The Stimela environment is built within Matlab/Simulink®, which is very well suited for mathematical models. Stimela models of drinking water treatment processes calculate changes of the water quality parameters, such as pH, oxygen concentration, DOC concentration etc. (<http://www.stimela.com>).

2.5 Fluidization modelling of ion exchange

Schagen *et al.* (2006) applied two general fluidization models of Ergun and Richardson-Zaki to explain the hydraulics of fluidization behaviour as in the following.

2.5.1 Ergun model

The porosity is determined by the balance between the pressure gradient over the fluidized bed due to the mass of the resins and the drag force of the water on the resin particle. The pressure gradient is given by the submerged weight of the resins:

$$\frac{\Delta P}{\Delta L} = (\rho_r - \rho_w)(1 - p)g \quad \text{Eq.6}$$

The pressure gradient caused by the drag force is derived from the drag force on one particle. Taking the porosity into account, the pressure gradient is given by:

$$\frac{\Delta P}{\Delta L} = \frac{3}{2} C_{wl} \frac{v^2}{2} \frac{1-p}{p^3} \frac{\rho_w}{d_r} \quad \text{Eq.7}$$

Where the drag force coefficient is determined by the following empirical formula:

$$C_{wl} = 2.3 + \frac{150}{\text{Re}_h} \quad \text{Eq.8}$$

where $C_{w1} \approx \frac{125}{Re_h^{0.8}}$ and $5 < Re_h < 100$

And

$$Re_h = \frac{2}{3} \frac{v d_r}{(1-p)v} \quad \text{Eq.9}$$

Combining Eq. 6, 7, 8 and 9, the porosity correlation is found:

$$\frac{p^3}{(1-p)^{0.8}} = 130 \frac{v^{1.2}}{g} \frac{v^{0.8}}{d^{1.8}} \frac{\rho_w}{(\rho_r - \rho_w)} \quad \text{Eq.10}$$

From this equation, the bed expansion porosity can be predicted. To apply this model, the Reynolds number has to be determined.

2.5.2 Richardson and Zaki model

Richardson and Zaki have introduced the relationship between the porosity and the fluidization velocity for the mono-sized particle bed as:

$$v = v_0 * p^n \quad \text{Eq.11}$$

Schiller and Naumann have presented a model to calculate the expansion index n by using the Galileo number (Nesbitt *et al.*, 1998):

$$n = \left[5.5 + 23 \frac{d_r}{D} \right] Ga^{-0.075}, (21 < Ga < 24,000) \quad \text{Eq.12}$$

$$Ga = \frac{d_r^3 g (\rho_r - \rho_w) \rho_w}{v^2} \quad \text{Eq.13}$$

They have also introduced a model for the calculation of the particle terminal velocity v_0 also using the Galileo number as:

$$Ga = 18 Re_0 + 2.7 Re_0^{1.687}, (3.6 < Ga < 10,000) \quad \text{Eq.14}$$

$$Re_0 = \frac{\rho_r d_r v_0}{\mu} \quad \text{Eq.15}$$

When the expanded bed porosity is known, the expanded bed height can be predicted:

$$H = \frac{H_0 (1 - p_0)}{(1 - p)} \quad \text{Eq.16}$$

Finally, it has to be considered that the fluidization only occurs when the particles can move freely in a horizontal plane with the minimum porosity of:

$$p_{\min} = 1 - \frac{\pi}{6} \approx 0.48 \quad \text{Eq.17}$$

If the fluidization models are valid for the ion exchange process, the expanded bed can be predicted. The height of fluidized ion exchange reactor can be designed.

3 Experiments with ion exchange resins

3.1 Materials and methods

3.1.1 Batch experiments

Resins

According to past research of Siegers *et al.* (1999) it is found that NOM that has a particle size between 100 to 1000 g/mol and neutral NOM have influence on the (GAC) by competition with pesticides. The large fraction of NOM fouls membranes and adsorbents (Bolto *et al.*, 2004). The aromatic fraction and unsaturated carbon fraction is known as the problematic compound for ozonation, and is a precursors for by-product formation. It would be an advantage when the resin could remove these NOM fractions. With help of literature and manufacturers information, four resins are selected to test specific NOM fraction removal.

Lewatit VP OC 1071

The Lewatit VP OC 1071 is a strong base, gel anion exchange resin (type I) based on an acryl-dyvilbenzene copolymer of special bead size distribution. It has high exchange capacity of 1.25 meq/ml. This resin is specially recommended for the removing of organic matter from surface water. It is expected to remove the high molecular weight fraction such as humic substances and aromatic NOM fraction. (<http://www.sybronchemicals.com/products/anions/vpoc1071.pdf>)

Purolite Macronet 200

Purolite Macronet 200 is a sorbent (not an ion exchange resin) and has a high internal surface area, and is highly rigidly cross-linked in swollen state. The sorbent has little or no change in swelling with change of the permeating liquid. The Purolite Macronet 200 is suitable for the sorption of high molecular weight NOM with lipophilic properties (fat-like). The sorbent is also recommended for the removal of hydrophobic NOM fraction. Moreover it is reported that this sorbent can also remove the complex organics such as dyestuffs (colour substances) and some pesticides. This sorbent is selected for removal of a hydrophobic NOM fraction. (<http://www.purolite.com/ProductID/310/FolderID/173/PageVars/Library/Products/ProductDetails.htm>).

Duolite A7

Duolite A7 is a weak base anion exchange resin and made from a cross-linked phenol-formaldehyde polycondensate. This resin is highly porous and has a high exchange capacity of 2.1 meq/ml. The resin characteristics are suitable for a small organic acid removal. Duolite A7 has good performance in organic acid removal when the influent water pH is in range of 0 to 6. (<http://www.rohmmaas.com/ionexchange>)

MIEX DOC

MIEX DOC is a magnetic ion exchange resin, which is specially produced for DOC removal. The resin bead of MIEX DOC is small, approximately 150 µm in diameter, and it provides a high exchange surface area and high exchange capacity. Chow *et al.* (2002) and Morran *et al.* (2004) have found that MIEX is the best resin in DOC removal that can provide approximately 85-90%. According to Fearing *et al.* (2004), the MIEX DOC is selected in order to remove the middle molecular weight fraction and aromatic NOM fraction.

(<http://www.miexresin.com/index.asp?page=9>)



Figure 5 The selected resins (Lewatit VP OC 1071, Purolite Macronet 200 and Duolite A7).

Table 2 Specification of selected resins.

Resin	Ionic	Pore	Structure	Type	Bead sizes µm	Capacity eq/L	% water content
Lewatit VP OC 1071	Cl	Gel	Acrylic	SB	400-1600	1.25	55-61
Purolite Macronet 200		Sorbent	Styrene		300-1200		55-62
Duolite A7		MP	Phenol formaldehyde	WB	600-800	2.1	54-64
MIEX DOC	Cl	MP	Acrylic	SB	150-180		

MP = Macro porous structure; SB = Strong base resin; WB = Weak base resin

Raw water

The used raw water is WPK water. The WPK water is mainly taken from the Bethune polder with high NOM content. The sample water is taken at the position after the pre-treatment process before the first post-treatment process (ozonation).

Measurement methods

DOC measurement

The DOC was determined as the non-purgeable organic carbon with an I.O. Analytical Model 700 Analyser by catalytic combustion/non-dispersive infrared gas analysis method.

UV absorbance

The UV absorbance measurements of the samples were performed with the Genesys 6 UV-Visible spectrophotometer (show in Figure 6), with split-beam and 1.8 nm spectral bandwidth. The absorbance values were measured with multiple wavelengths of 230 nm, 254 nm and 280 nm.



Figure 6 The Genesys 6 UV-Visible spectrophotometer.

Fluorescence excitation emission matrix

The fluorescence EEM is conducted with the FluoroMax-3, as show in Figure 7, which is a spectrofluorimeter from JY-Horiba that is applicable to multiple fluorescent intensity measurements. The fluorimeter follows a classical configuration with a Xenon arc lamp, excitation and emission mono chromators before and after the sample, a photomultiplier tube (PMT) for detection and a reference photodiode.

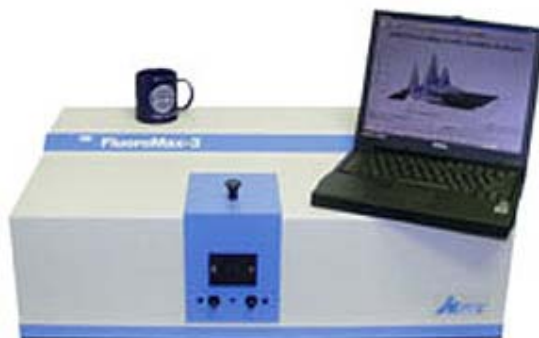


Figure 7 The FluoroMax-3 from Horiba Jobin Yvon.

Liquid Chromatography - Organic Carbon Detection

At present, the LC-OCD-technique is the analytical technique to characterize and quantify non-volatile, hydrophilic organic compounds in waters. The technique was developed by a small private Company in Karlsruhe (Grüntzel Co.), together with the University of Karlsruhe (Engler-Bunte-Institute) in the years 1985-1990. The instruments are shown in Figure 8.



Figure 8 The LC-OCD of DOC-LABOR Dr HUBER.

Temperature, pH and conductivity

The temperature, pH and conductivity are measured with the multi 350i handheld meter from the WTW GmbH.

3.1.2 Fluidization experiments

Resin

The Lewatit VP OC 1071 is a strong base, gel anion exchange resin (type I) based on an acryl-dyvilbenzene copolymer. It has a high total exchange capacity. This resin is specially recommended for the removal of organic matter from surface water. According to results of the study on NOM fraction removal, this resin is the most suitable for the implementation in WPK drinking water treatment plant, Amsterdam. This resin is chosen for the fluidization research.

Feed water

Tap water is used as the feed water. The tap water contains low NOM concentrations (the tap water is selected, as feed water in order to make sure that there is as little as possible ion exchange in the test column). This experiment is concentrated on the result of the hydraulics of resin fluidization, when ion exchange occurs it might have an influence on the resin density and size.

3.2 Experimental setup

3.2.1 Batch experiments

The batch experiments are applied for the study of ion exchange kinetics (linear driving force model) and the equilibrium of ion exchange (Freundlich Isotherm) of all selected resins.

Ion exchange kinetics

All selected resins are dosed with an amount of 160 mg/l resin in a glass vessel with a volume of 2 litres. The raw water without resin is also set in order to compare the

change of water quality in time. The glass vessels are continuously stirred. The eight measurements are carried out in time. There are two samples of the weak base resin Duolite A7. One is a sample with the pH adjustment to 5 and another is measured at natural raw water pH=7.8. The setting is shown in Figure 9.



Figure 9 The batch experiment setting: Ion exchange isotherm.

The temperature is controlled at 16°C and the pH is measured on a daily basis. The sample is analyzed with DOC detection, UV absorbance, fluorescence EEM and LC-OCD to explore both kinetics of ion exchange and NOM fraction removal. The samples for DOC detection, UV absorbance and fluorescence EEM were taken in time at 6, 29, 50, 122, 172, 220, 293 and 337 hours with a syringe volume of 10 ml and immediately filtrated with a cellulose acetate filter pore size 0.45 μm . The samples for LC-OCD were taken at 337 hours with a syringe without filtration. The sample glass bottles are first cleaned with alkaline detergent 5% and after that cleaned with the solution NaOH 5 M for 2 hours and then with HCL 5 M for 2 hours. Finally the bottles were cleaned and rinsed many times with demi-water.

Equilibrium study

The equilibrium of ion exchange is described using the Freundlich isotherm approach. The experiment was set with eight different resin dosing amounts. There are approximately 10, 20, 40, 80, 160, 320, 640 and 1,280 mg/l resin in a glass vessel volume of 1 litre. The setting is shown in Figure 10. The temperature is controlled at 16 °C, the pH is not controlled for Lewatit VP OC 1071, Purolite Macronet 200 and MIEX DOC. For the weak base resin Duolite A7 one set, the pH is adjusted to approximately 5 and another set the pH is not controlled. The measurement is done at 14 days residence time (the end of experiment) when expected the equilibrium of ion exchange. The samples are taken with a syringe volume of 10 ml and immediately filtrated with a cellulose filter pore size 0.45 μm . DOC concentration, UV absorbance and fluorescence EEM are applied for the analysis step.



Figure 10 The batch experiment setting: equilibrium of ion exchange set up.

For all experiments, the Lewatit VP OC 1071 and the Duolite A7 are first regenerated with the solution of 10% NaCl and 2% NaOH. The Purolite Macronet 200 is regenerated with a methanol-MeOH solution. In order to make sure that the resins are completely regenerated, the resin is added into the regenerant for 12 hours. After regeneration the resins are rinsed many times with demi-water. The MIEX DOC used is a virgin resin.

3.2.2 Fluidization experiments

In this experiment, it is assumed that both resin density and the resin diameter are constant and there is no ion exchange. The diameter of resin is analysed using the wet sieve analysis method.

Particle size distribution

The particle size distribution is carried out using the wet sieve analysis method. According to the manufacturers resin specification, the Lewatit VP OC 1071 resin has particle size range from 400 μm to 1,600 μm . The effective size is 550 μm $\pm$ 50 μm . The sieve meshes used have diameter size of 900 μm , 800 μm , 710 μm , 630 μm , 500 μm and 320 μm . Since the Lewatit VP OC 1071 is a gel resin, it gives poor result with the normal sieve method. In the wet situation, it is likely to give better results. To ensure the accuracy, the analysis is repeated 5 times.

The particle terminal velocity

To apply the Richardson-Zaki model, the terminal velocity has to be estimated first. The terminal velocity can be determined with the Schiller and Naumann model. This experiment is applied in order to check if the Schiller and Naumann model for terminal velocity is valid for an ion exchange resin. The experiment is carried out in a 0.5 m high glass tube with diameter of 0.08 m. The falling velocity is calculated by measuring the time it takes the resin particle to fall from the top to the bottom of the tube, divide by the falling distance. To ensure the accuracy, the measurement is repeated many times and only the particles that maintained a prescribed distance from the tube wall are recorded. At the end there were 13 useful measurements.

The expansion of resin bed

The setup for the resin expansion test consisted of a 2 m high column with diameter of 0.05 m. The resin is placed on small gravel at the bottom to prevent leakage of resin. The Lewatit VP OC 1071 is tested with several bed heights, to find the relation between the expanded bed height and the vertical flow velocity. The tap water is fed into the column via the control valve through a flow meter. The effluent is released to the sewerage system. The temperature and pH is regularly measured from the effluent flow. The setup is shown in Figure 11.

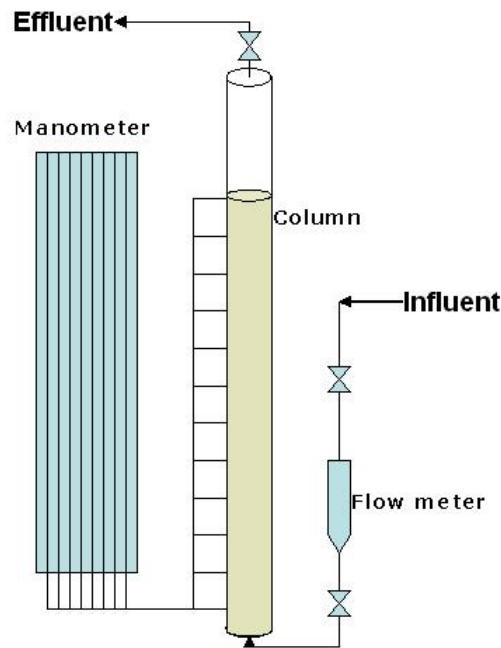


Figure 11 The fluidized ion exchange experiment setup.

The pressure drop

The pressure drop data are collected from the manometer tubes. The tubes are connected to the test column at the heights of 0.1, 0.2, 0.3, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.3 and 1.5 m. According to the equation 6, the expanded porosity of resin bed can be determined from the pressure drop.

4 Results and discussions

4.1 Characterization of Weesperkarspel natural organic matter

WPK NOM is characterized with the UV absorbance measurement, DOC, Fluorescence EEM and LC-OCD. The results are shown in Table 3 and Figure 12, 13 and 14. UV absorbance analysis shows that WPK NOM can absorb highest amount of UV₂₃₀ of 36.7 ext/m, UV₂₅₄ at 21.2 ext/m and UV₂₈₀ at 16 ext/m. When UV₂₃₀ absorbance is the indicator for organic nitrogen, it shows that WPK water contains high amount of this fraction. And when the UV₂₅₄ and UV₂₈₀ absorbance is representative for the aromatic NOM fraction, the results are shown that for both wavelengths for WPK NOM performed high amount of the UV absorption. The WPK NOM contains high degree of aromatic NOM fraction.

Table 3 Results of UV, DOC, and SUVA measurement of raw WPK water.

Analysis method	Unit	WPK
UV ₂₃₀	ext/m	36.7
UV ₂₅₄	ext/m	21.2
UV ₂₈₀	ext/m	16.0
DOC	mg C/l	7.2
SUVA ₂₅₄	l/(mg C*m)	2.94

The DOC concentration of WPK NOM is reported as 7.2 mg C/l. For the WPK drinking water treatment plant, NOM is mainly removed with BAC. This high concentration of DOC might be the origins of BAC filter rapidly saturation.

The last characterization method is the SUVA₂₅₄ value (shown in Table 3). SUVA₂₅₄ of WPK NOM is calculated at 2.94 l/mg C m. At this SUVA₂₅₄, the WPK NOM is indicated to the mixture of hydrophobic with hydrophilic NOM fraction.

For more informative WPK NOM fractionation analysis, the results of fluorescence EEM are shown in Figure 12 in form of the contour picture of fluorescence absorption intensity of WPK water as a function of excitation and emission wavelength. There are 2 peaks of adsorption intensities found. The first peak is located at excitation wavelength of 300 nm combined with an emission wavelength of 430 nm. Based on the fluorescence EEM NOM fractions characterization of Chen *et al.* (2003), this peak is located in the humic acids-like NOM fraction region. The second peak is located at the same emission wavelength combined with 250 nm of excitation wavelength. This peak has about two times higher intensity than the first peak. This peak can be indicated as the fulvic acids-like fraction. However, both humic acids and fulvic acids are parts of the humic substance NOM fraction, which have a small difference in their solubility properties. There is no peak found in neither the proteins-like or the microbial by-products-like region.

Hence, the conclusion of fluorescence EEM of WPK NOM is that WPK water contains high amounts of humic substances fraction and this fraction can be characterized into fulvic acids and humic acids. The fulvic acids-like NOM can absorb about double the intensity of fluorescence light compared to humic acids-like.

The fluorescence EEM results describe only which possible compound group is present in the sample. The concentration of humic substance is analysed further with the LC-OCD method.

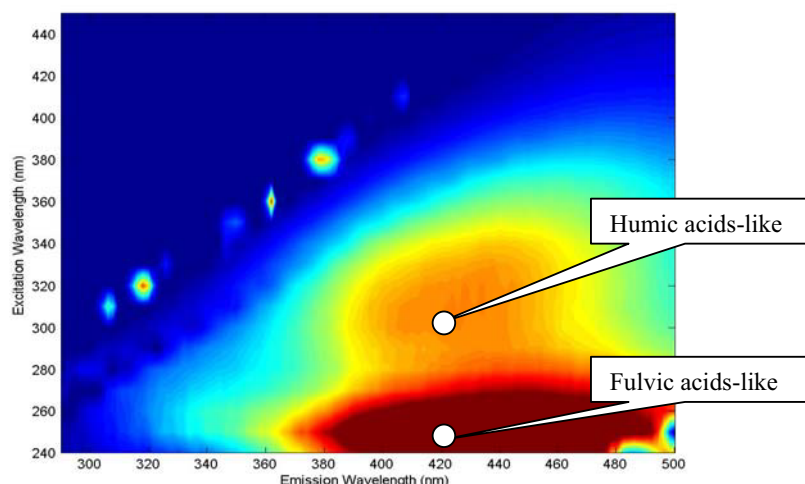


Figure 12 The fluorescence EEM contour picture of WPK NOM.

Recently, the LC-OCD method has become popular for NOM characterization because it gives quantitative information about compound components. The LC-OCD results of WPK NOM are shown in Figure 13 and 14. The DOC concentration is 5.73 mg C/l and fractionated to a biopolymers concentration of 0.066 mg C/l (1.2%), a humic substances concentration of 3.895 mg C/l (67.9%), a building blocks concentration of 0.901 mg C/l (16.1%) and a neutrals of 0.608 mg C/l (10.2%). The low molecular weight organic acids have not been found in WPK water.

The DOC concentration measured with LC-OCD methods is lower than measured with the TOC detector I.O. Analytical Model 700 Analyser. The sample preparation of both analysis methods is different. A difference in sampling time, samples of LC-OCD were taken two week later from the DOC measurement. Moreover the different analysis methods might lead to the differences in DOC results.

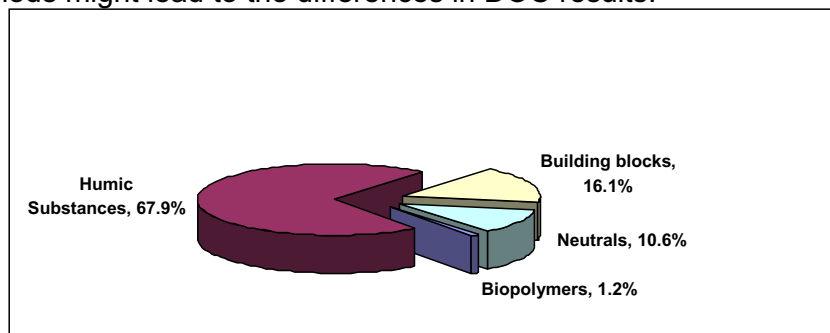


Figure 13 The DOC component of WPK NOM.

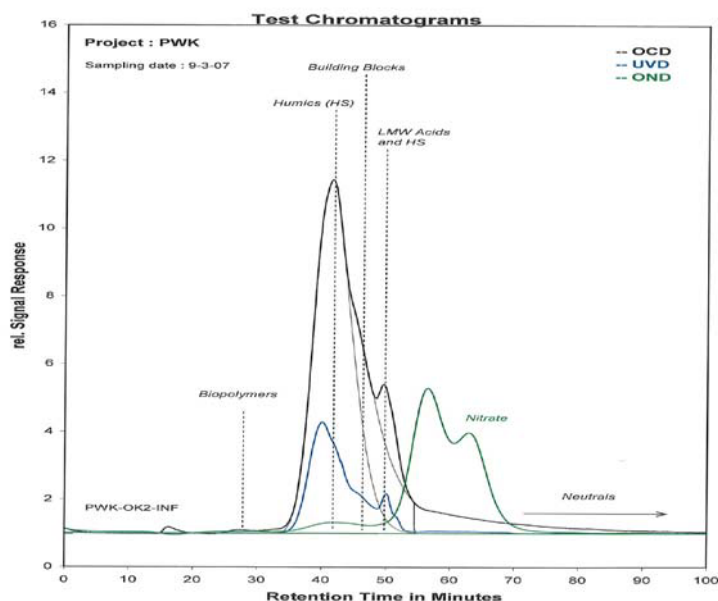


Figure 14 The test chromatogram of NOM of WPK water.

By combination of UV, DOC, SUVA, fluorescence EEM and LC-OCD results, the composition of WPK NOM is:

1. DOC concentration of 7.2 mg C/l (according to DOC measurement).
2. DOC of WPK resource contains high degrees of humic substances of 67.9%.
3. Humic substances consisted of humic acids-like and fulvic acids-like fraction.
4. High degree of an aromatic compound.
5. The organic nitrogen is an important fraction of WPK NOM

4.2 Natural organic matter fractions removal with ion exchange resins

The treated water with different ion exchange resins took place after two weeks of residence time of 160 mg/l resin concentration. The removal results are shown in Table 4, 5 and 6. The complete measurement data are shown in appendix 1.

Table 4 The decreasing results of UV, DOC and SUVA measurement.

Resins	UV						DOC		SUVA ₂₅₄	
	230 nm		254 nm		280 nm					
	ext/m	% Decrease	ext/m	% Decrease	Ext/m	% Decrease	Mg C/l	% Decrease	I/(mg*m)	% Decrease
WPK	36.70		21.20		16.00		7.20		2.94	
Lewatit VP OC 1071	17.20	53.13	7.50	64.62	6.30	60.63	3.40	52.78	2.21	25.08
Purolite Macronet 200	34.80	5.18	19.90	6.13	15.10	5.63	7.20	0.00	2.76	6.13
Duolite A7 pH=5	29.00	20.99	13.40	36.79	10.30	35.63	4.90	31.94	2.73	7.12
Duolite A7 pH=7.8	35.60	3.00	20.40	3.77	15.30	4.38	6.70	6.94	3.04	-3.41
MIEX DOC	19.80	46.05	9.20	56.60	7.50	53.13	4.00	44.44	2.30	21.89

Table 4 shows the results of UV absorbance, DOC measurement and the calculated SUVA₂₅₄ of treated WPK water with different ion exchange resins. It can be observed that Lewatit VP OC 1071 decreased the highest percentage of all UV wavelengths, DOC and SUVA₂₅₄. The Lewatit VP OC 1071 decrease about 65% of UV₂₅₄, which can be contributed to the aromatic NOM fraction. DOC is 53% reduced and the reduction of SUVA₂₅₄ at 25%. The SUVA₂₅₄ was remaining at value 2.22. This value shows that the most of humic substances has been removed and the remained NOM has shown a hydrophilic property. The organic nitrogen fraction (indicated by UV₂₃₀) is decreased also more than 50%.

The MIEX DOC had also good removal performance. It decreased high amounts of all UV wavelengths, DOC and SUVA₂₅₄ but less than the Lewatit VP OC 1071. The SUVA₂₅₄ remained at higher value meaning that it less removed of the high molecular weight NOM fraction.

The Duolite A7 with low pH (pH=5) decreased 21%, 37% and 36% of UV₂₃₀, UV₂₅₄ and UV₂₈₀ respectively. The DOC concentration is decreased with 31%. The SUVA₂₅₄ is slightly decreased. It can be noticed that the weak base Duolite A7 (pH=5) can remove rather high amounts of aromatic NOM fraction (UV₂₅₄).

The weak base Duolite A7 in normal raw water (pH=7.8) is apparently not active. It decreased only low percentages of all UV wavelengths, DOC and SUVA₂₅₄.

The results of raw water treated with the sorbent Purolite Macronet 200 show only about 5-7% of decrease.

Although, the fluorescence light absorbance intensity is not able to indicate directly the NOM fraction quantities, the fluorescence light absorbance comparison between the raw water and the treated water can give some information of the NOM fraction decrease. Figure 12 has shown that humic substances NOM fraction consisted of humic acids-like and fulvic acids-like fractions.

Table 5 The fluorescence EEM results.

Resins	Fluorescence EEM			
	Humic acids-like		Fulvic acids-like	
	Intensity	% Decrease	Intensity	% Decrease
WPK	5153437	-	10361353	-
Lewatit VP OC 1071	1525785	70.39	2476706	76.10
Purolite Macronet 200	4540287	11.90	9077040	12.40
Duolite A7 pH=5	3778021	26.69	8353961	19.37
Duolite A7 pH=7.8	6099721	-18.36	11458357	-10.59
MIEX DOC	2836218	44.96	3951709	61.86

By comparison at the same excitation and emission wavelength where the peaks are located, the percentage of decrease is determined as shown in Table 5. The fluorescence EEM contour pictures of all resins are shown in appendix 2. The Lewatit VP OC 1071 performed best in both sub-humic substances NOM fraction removal. The humic acids-like NOM fraction is about 70% decreased while fulvic acids-like NOM fraction is reduced about 76%. The MIEX DOC resin decreased humic

substance NOM fraction with about 45% of humic acids-like and 62% of fulvic acids-like NOM fraction.

The weak base Duolite A7 in acid pH=5 decreased with 27% and 19% of the humic acids-like and fulvic acids-like respectively while in the normal raw water, an increasing of these two NOM fractions is observed.

The sorbent Purolite Macronet 200 absorbed both humic acids-like and fulvic acids-like NOM fractions with about 12%. It shows that the adsorption removed less NOM than with the electrostatic interaction (Ion exchange mechanism).

The DOC of WPK water is separated into 4 NOM fractions with LC-OCD, with this analysis method more information about DOC fraction removal is determined. The LC-OCD results of raw WPK water and treated water are shown in Table 6.

Table 6 LC-OCD results.

Resins	LC-OCD							
	Biopolymers		Humic substances		Building blocks		Neutrals	
	mg C/l	% Decrease	mg C/l	% Decrease	mg C/l	% Decrease	mg C/l	% Decrease
WPK	0.07	(1.1% DOC)	3.90	(66.3% DOC)	0.91	(15.7% DOC)	0.61	(10.4% DOC)
Lewatit VP OC 1071	0.01	78.79	0.23	94.17	0.82	10.53	0.40	34.54
Purolite Macronet 200	0.04	40.91	3.78	2.85	0.88	3.84	0.48	20.39
Duolite A7 pH=5	0.06	4.55	2.13	45.37	0.81	10.96	0.61	-0.66
Duolite A7 pH=7.8	0.04	43.94	3.78	2.93	0.89	1.97	0.65	-6.91
MIEX DOC	0.03	59.09	1.18	69.65	0.67	26.97	0.47	22.20

Table 6 shows that the Lewatit VP OC 1071 performed best in WPK NOM removal. The removal of humic substances NOM is almost complete (94%). The neutrals NOM fraction is also higher removed compared with other resins. To remove this neutral NOM fraction, an absorption mechanism is required. It means that the absorption mechanism is involved in the removal process of the Lewatit VP OC 1071. The MIEX DOC performed constantly in the second place. This resin removed highest amount of building block NOM fraction. The absorption is also involved in the MIEX DOC removal process. The weak base Duolite A7 pH=5 removed about 45% of the humic substance NOM fraction but it cannot remove any of the neutral NOM fraction. When the pH is high (pH=7.8), the weak base Duolite A7 is able to remove only the biopolymer NOM fraction. The sorbent Purolite Macronet 200 removed only the biopolymer and neutral NOM fractions.

The sorbent Purolite Macronet 200 is able to remove the biopolymer NOM fraction that is the highest molecular weight NOM fraction. For removal the large NOM fractions the absorption process is required. The biopolymer NOM fraction removal results of the weak base Duolite A7 in normal raw WPK water is evident. At the pH of 7.8, this resin is not able to dissociate, meaning that no ion exchange occurred, only adsorption took place as the removal process and it removed about 43% of this large molecular weight NOM fraction.

In LC-OCD analysis methods, the specific SUVA of humic substances is also calculated. With this figure, the average molecular weight of humic substances can be determined. The SUVA value and the molecular weights of humic substances are shown in Table 7.

Table 7 The SUVA value and molecular weight of humic substances.

Resins	SUVA	MW
	l/(mg*m)	g/mol
WPK	3.42	712.00
Lewatit VP OC 1071	1.98	737.00
Purolite Macronet 200	3.50	718.00
Duolite A7 pH= 5	2.02	608.00
Duolite A7	3.46	712.00
MIEX DOC	1.29	483.00

Although the Lewatit VP OC 1071 can remove humic substance NOM fraction almost completely, the molecular weight of this fraction is increased. The removed part of humic substances seems to be only a low molecular weight NOM fraction. The molecular weight of humic substances of treated water with MIEX DOC is lowest. The high molecular weights humic substances might be removed. The same as occurred with the weak base Duolite A7 pH=5. The high molecular weights parts seem to be removed.

The resin structure might be the dominant parameter for the NOM removal. The gel resin Lewatit VP OC 1071 performs better than the macroporous resin the MIEX DOC and Duolite A7. The diffusion resistance seems to be an important parameter for humic substances removal. A smaller resin bead size of MIEX DOC, which is about 3 times smaller than the gel resin Lewatit VP OC 1071, removed lower amounts of humic substances NOM fraction.

WPK NOM contains a high amount of a high molecular weight NOM fraction as a humic substance. For the removal of high molecular weight NOM fractions like humic substances, the gel resin structure can perform better than macroporous resin. The experiment results of Croue *et al.* (1999) with [Dowex MSA-1, Dowex 11 and IMAC HP661] and Tan *et al.* (2005) [Dowex Marathon A, Dowex 22 and Dowex M-43] have the same results. They concluded that the gel resin is most effective in NOM removing compared to strong base macroporous and weak base macroporous resins.

The strong base resin Lewatit VP OC 1071 and the MIEX DOC removed higher amounts of WPK NOM than the weak base Duolite A7. The strong base is able to give an ion in the whole pH range while the dissociation of weak base is limited with pH value. The weak base Duolite A7 performed good in WPK NOM removal when the water pH is 5. It seems not to exchange any ions when the pH value is nearly 8. Several researchers have also concluded that the strong base resin performs better than weak base resin in NOM removal (Tan *et al.*, 2005; Bolto *et al.*, 2004; Croue *et al.*, 1999).

By adsorption, the large molecular weight NOM fractions like biopolymers can be removed. The results of biopolymer fraction removal of Purolite Macronet 200 and

Duolite A7 confirm this. Bolto *et al.*, (2004) have also found that the adsorption is dominant over electrostatic interaction in the removal of larger NOM fractions.

The sorbent Purolite Macronet 200 can remove high percentages of NOM when the adsorption process takes place.

In this thesis study, the non-removed DOC is also determined by using of different amounts of resin dosing varied from 10 mg/l to about 1280 mg/l. The non-removable DOC is one of the necessary parameters for the suitable resin selection for WPK NOM removal. The results of the non-removable DOC are shown in Table 8 and Figure 15.

Table 8 Non-removable DOC.

Resin	Non removable DOC	
	mg C/l	%
Lewatit VP OC 1071	2.3	31.9
Purolite Macronet 200	6.8	94.4
Duolite A7 pH=5	3.9	54.2
Duolite A7 pH=7.8	7.2	100.0
MIEX DOC	3.1	43.1

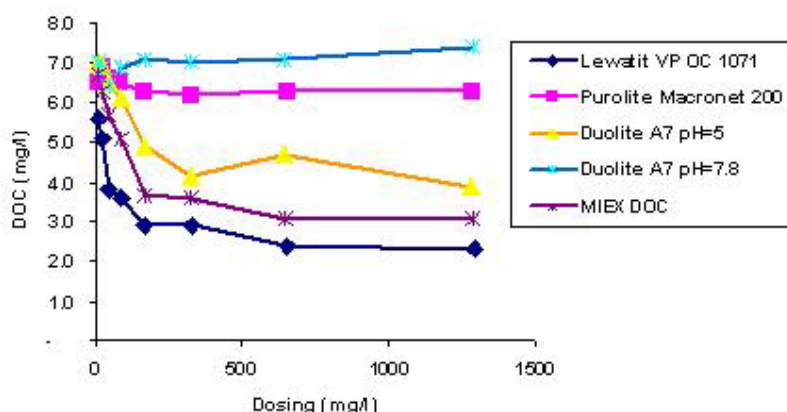


Figure 15 The DOC removal respect of resin dosing.

The results show that the treated water with Lewatit VP OC 1071 has the lowest non removable DOC. It is about 32% of the initial DOC. The MIEX DOC has a non-removable part of about 43% DOC. The weak base Duolite A7 in the WPK water with pH adjusted to 5 performed rather well. There is about 54% non-removable DOC remained. The DOC concentration of treated water with Duolite A7 in normal WPK water is almost constant at the same level of raw WPK water. The DOC concentration of treated water with sorbent Purolite Macronet 200 remained at 6.8 mg C/l or about 94% left. Figure 15 shows the decrease of DOC concentration with respect to resin dosing. It is observed that at resin dosing about 650 mg/l, the removal of DOC of all resins has reached the maximum.

4.3 Mathematical modelling of ion exchange

4.3.1 The kinetics of ion exchange

The kinetic removal of UV_{254} absorbance of treated WPK water with ion exchange resins concentrations of 160 mg/l are shown in Figure 16.

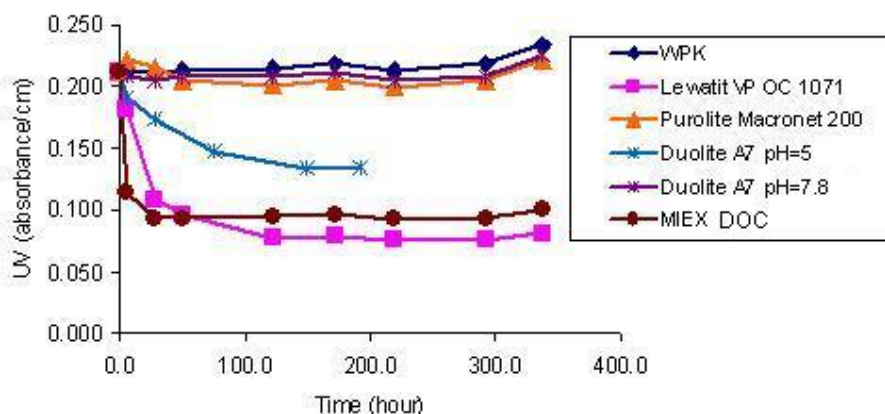


Figure 16 The kinetic UV_{254} absorption with different resins.

The results show that the UV_{254} absorbance decreased rapidly with time for the MIEC DOC. After 6 hours of residence time, it almost reaches the maximum removal point. The reduction of UV_{254} absorbance of the Lewatit VP OC 1071 is slower than the MIEC DOC. It took about 125 hours to reach the maximum removal. The weak base Duolite A7 in low pH water requires about 150 hours of residence time to reach the maximum removal point.

With the help of the linear driving force model, the kinetics of ion exchange can be described. According to Eq.3 and exponential form Eq.4, the ion exchange isotherm and the LDF- k constant can be determined with batch experiments.

In case of the sorbent Purolite Macronet 200 and the weak base Duolite A7 in normal raw water, only small removals are observed. Therefore, the LDF- k constant cannot be determined.

Based on the UV_{254} absorbance results, the LDF- k constant is determined by plotting $\ln[C_0 - C_e]/(C_t - C_e)$ against the residence time in hours. The LDF- k constant is determined from the slope. Figure 17 shows the conversion of Figure 16 into the exponential form according to Eq.4.

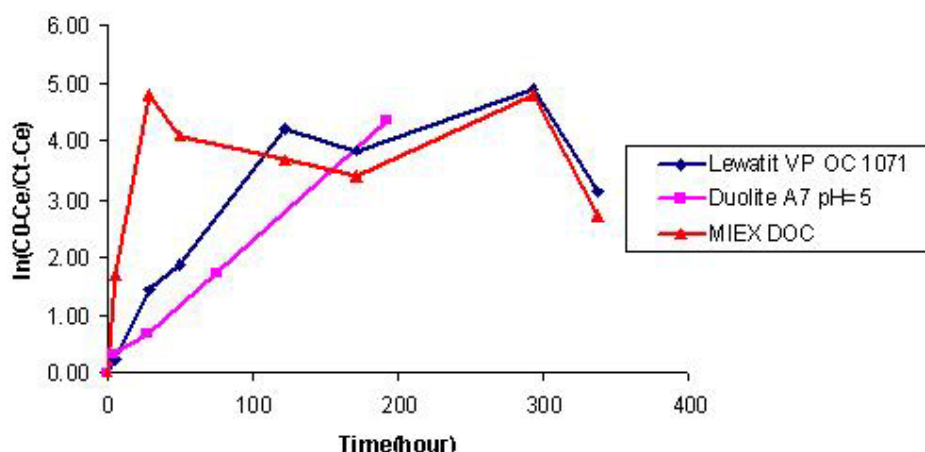


Figure 17 The kinetic UV_{254} absorbance removal in exponential form according to Eq.3.

The LDF- k constant is related to ion exchange rate, this value can be determined only from data before the ion exchange process reaches the maximum exchange. Thus, the calculation of LDF- k constant used only 3 measurement data of the MIEX DOC, 4 measurement data of Lewatit VP OC 1071 and Duolite A7. The LDF- k constant values are shown in Table 9.

Table 9 The LDF- k constant of different resins.

Resin	LDF- k (h^{-1})	R^2
Lewatit VP OC 1071	35.7	0.98
Duolite A7 at pH=5	23.1	0.97
MIEX DOC	169.9	0.96

According to Eq. 4, an increase of LDF- k constant means that the resin has a higher ion exchange rate. The exchange reaches faster the maximum removal or equilibrium point. The results in Table 9 shows that MIEX DOC with a LDF- k constant of $169.9 h^{-1}$ can decrease UV_{254} absorbance faster than the other resins. Although the Lewatit VP OC 1071 decreased the highest percentage of UV_{254} absorbance, the LDF- k constant is only $35.7 h^{-1}$. Because of this lower LDF- k constant, the resin requires more time to reach the equilibrium. The weak base Duolite A7 resin also requires longer time for the ion exchange process because of low LDF- k constant of $23.1 h^{-1}$.

The differences of ion exchange rate might be a result of difference in the resin properties. The resin bead size can be the reason. The MIEX DOC has the smallest size of $150 \mu m$. Lewatit VP OC 1071 has effective bead size of $550 \mu m$ and the Duolite A7 has bead size of about $700 \mu m$.

However, this result is based on the resin dosing of about $160 mg /l$. The ion exchange rate is also dependent on the dosing. Whenever the dosing is higher, the graph might be shaper and the LDF- k constant will be larger because the exchange sites are increased and the driving force is increased.

4.3.2 The equilibrium of ion exchange

With the assumption that the released ion from the resin has no effect on the ion exchange process and the resin is unchanged, the equilibrium state of ion exchange can be described. Freundlich constant K and n can be determined from the batch experiment by varying the resin dosing from about 10 mg/l to about 1,280 mg/l. The data of DOC removal of Figure 15 is used to determine the Freundlich constant K and n for all ion exchange resins. $\ln(Q_e)$ is plotted against $\ln(C_e)$. The Freundlich constant K is determined from the intersection on the Y-axis and the n is slope of the graph.

Whenever the decreasing of DOC is not observed, the Freundlich constant cannot be determined. Therefore, the Purolite Macronet 200 and the Duolite A7 in normal raw WPK water has no Freundlich isotherm. The calculation of Freundlich constant is shown in Figure 18 and the calculation results are shown in Table 10.

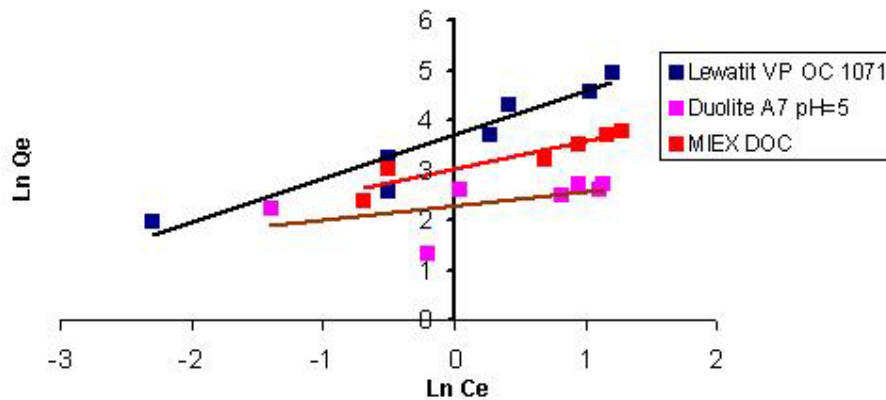


Figure 18 The determination of Freundlich constant K and n

Table 10 The Freundlich isotherm constant K and n of different ion exchange resin.

Resin	K $\text{g/kg} \cdot (\text{m}^3/\text{g})^n$	n	R^2
Lewatit VP OC 1071	40.13	0.87	0.90
Duolite A7 pH=5	4.39	0.79	0.82
MIEX DOC	20.49	0.55	0.86

According to the Eq.5, the Freundlich constant K and n are dependent parameter. Both constants together describe the exchange capacity of the ion exchange resin. In order to compare the exchange capacity of these 3 resins, the breakthrough curve is calculated using the Stimela model. The LDF- k constant of each resin is also taken into account. The input data for Stimela model is shown in Table 12. This data is based on the designed treatment condition at WPK drinking water treatment plant, Amsterdam (explained in chapter 5). The water flow is about 4,000 m^3/h , the ion exchange reactor is designed of 20 reactors and the feed velocity is 20 m/h.

Table 11 The input parameter for the breakthrough curve calculation.

Flow per reactor	200	m ³ /h
Temperature	22	°C
DOC concentration	7.2	mg C/l
Filter surface area	10.00	m ²
Bed height	2	m
Porosity	50	%
Resin density	1,090	kg/m ³

In addition, the resin characteristics data's are collected from Table 2, 9, and 10. The non-removed DOC is not applied in order to get better comparison results of the influence of Freundlich constant K and n on the breakthrough curves. The breakthrough curves derived from the Stimela model are shown in Figure 19.

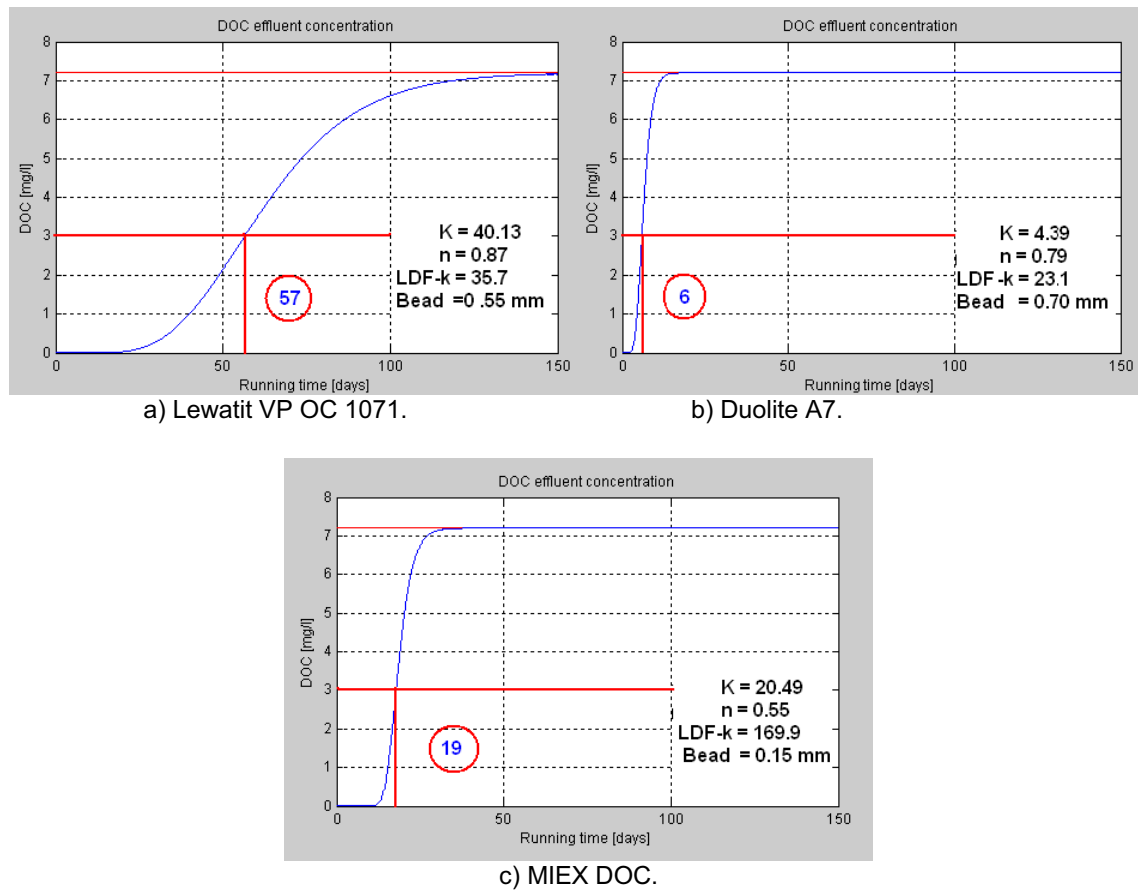


Figure 19 Breakthrough curves of 3 different resins.

As been mentioned the Freundlich constant K and n are dependently parameters which can describe the ion exchange capacity. Whenever, K and n value are larger, meaning that the running time before reaching the regeneration point, will be longer. According to the breakthrough curve results in Figure 19, the K value has influence to the shifting of the breakthrough curve graph to the right side and the n value has influence to the S-shape curve. When the regeneration process takes place at the

effluent DOC concentration of 3 mg C/l, it can be noticed that the Lewatit VP OC 1071, the highest value of both Freundlich constant K and n resin, has longest running time of 57 days before reaching the regeneration point. The effluent DOC concentration of treated water with the MIEX DOC increased to 3 mg/l within 19 days while the weak base resin Duolite A7 has shortest running time of 6 days. The exchange capacity of Lewatit VP OC 1071 is largest compared with MIEX DOC and Duolite A7 (this exchange capacity also can be observed in Figure 15 and 16 that DOC and UV₂₅₄ absorbance is highest decreased with resin Lewatit VP OC 1071). The breakthrough curve results are confirmed that the gel resin Lewatit VP OC1071 is the most suitable resin for WPK NOM removal.

4.4 Fluidization modelling of ion exchange

4.4.1 Resin bed characteristics

Resin bed porosity (p_0)

Assuming that the resin diameter does not change when it gets wet, the fixed bed porosity of the wet resin is equal to the dry resin. The resin bed porosity (p_0) is determined from the resin specification data of the manufacturer, using the shipping weight 730 g/l and the resin density of 1,090 g/l.

$$\text{ShippingWeight} = (1 - p_0) \rho_r \quad \text{Eq.18}$$

The porosity of the resin bed is calculated as 0.3303.

Effective particle size (d_r)

According to the resin specification, the Lewatit VP OC 1071 has a high uniformity coefficient of 1.80, means that the resin has a large distribution range of particle sizes. The manufacturer reports bead sizes in a large range between 400 – 1,600 μm and the effective bead size is 550 +/- 50 μm . A sieve analysis is carried out measuring the particle distribution, effective particle size and the uniformity coefficient of the wet resin. The results are shown in Figures 20. The resin samples were analysed for 5 times as shown in different coloured lines.

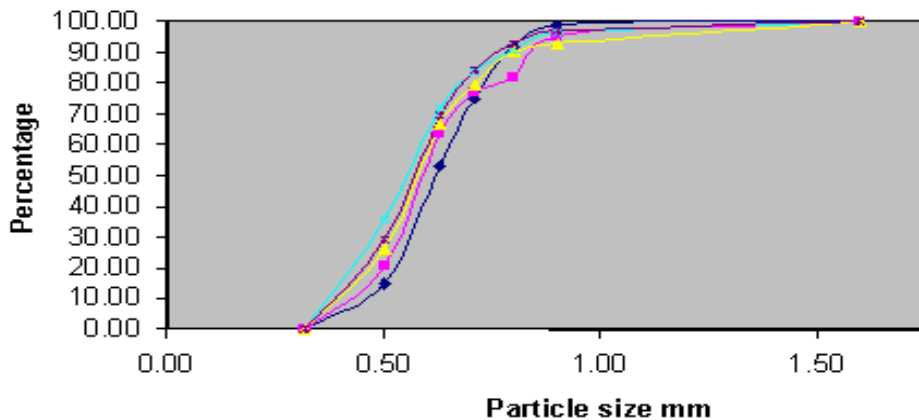


Figure 20 The cumulative particle size distribution curve of wet resin.

Figure 20 shows that most resin particles have a size between 0.5 to 0.63 μm and that this range of size contains about 40% of total particles. The particle size of 0.32 to 0.50 mm also contains a high percentage of about 20%. The D_{10} , D_{50} and D_{60} are determined and the uniformity coefficient of resin bead can be calculated with Eq.19. The average values of all parameters are shown in Table 12.

$$U = \frac{D_{60}}{D_{10}} \quad \text{Eq.19}$$

Table 12 D_{10} , D_{50} , D_{60} and uniformity coefficient of wet resin.

D_{60}	D_{50}	D_{10}	U
μm	μm	μm	-
608	564	402	1.52

A uniformity coefficient value of 1.52, means that the particle of wet resin becomes more uniform than the dry resin (1.80). When the D_{50} is considered as the effective size, the D_{50} of wet resin is 564 μm which is close to the dry effective size of 550 μm . This figure shows that the resin is swollen after absorbing some water into the bead. The swelling of resin resulted in a more homogenous bead size. Although it is reported that gel resin is swollen in wet condition, the changing in enlargement of effective bead size remained only at 1.62% (comparison of dry effective size of 550 μm and wet effective of size 564 μm). According to the sieve analysis results, it can be concluded that there is small/no change in resin bead size.

Wet resin density (ρ_r)

Although the resin diameter is not much changed when it gets wet, the mass of wet resin is apparently increased. The gel resin Lewatit VP OC 1071 has properties to adsorb water in the particle therefore the resin becomes heavier. It is necessary to find the wet density of resin for the model prediction. The measurements are done with the wet resin after 20 minutes in water. The wet density is found as average 1681 g/l with the dry porosity (0.3303) is taken into account (shown in Table 13).

$$\rho_r = \frac{m}{V(1-p)}, p = 0.3303 \quad \text{Eq.20}$$

Table 13 The density of wet resin.

Test	Mass	Volume	Density
	g	ml	g/l
1	46.71	40	1,743.7
2	44.86	40	1,674.6
3	44.14	40	1,647.8
4	44.01	40	1,642.9
5	46.10	40	1,720.9
6	44.41	40	1,657.8
Average			1,681.3

4.4.2 Testing of terminal velocity model of Schiller and Naumann

The terminal velocity data of different resin bead sizes were measured in the laboratory. The different resin bead sizes were collected from wet sieve analysis. The resulting data is shown in Table 14.

Table 14 The measured terminal velocity of different resin bead sizes.

ParticleSize(d_r)	Terminal Velocity (v_0)	
Diameter (μm)	(m/s)	Average (m/s)
320	0.010-0.013	0.012
500	0.015-0.024	0.018
630	0.025-0.031	0.027
710	0.028-0.033	0.031
800	0.032-0.040	0.035
900	0.036-0.050	0.041

For the application of Schiller and Naumann terminal velocity model (Eq.13, 14 and 15), the temperature of the experiment is determined: 21.20 °C. Table 15 shows the parameters that applied for the model. And Figure 21 shows the prediction results of the terminal velocity model compared with average measured terminal velocity data.

Table 15 The parameters for Schiller and Naumann model prediction.

Column diameter	0.05	m
Resin density	1,681	kg/m ³
Water density	1,000	kg/m ³
Temperature	21.2	°C

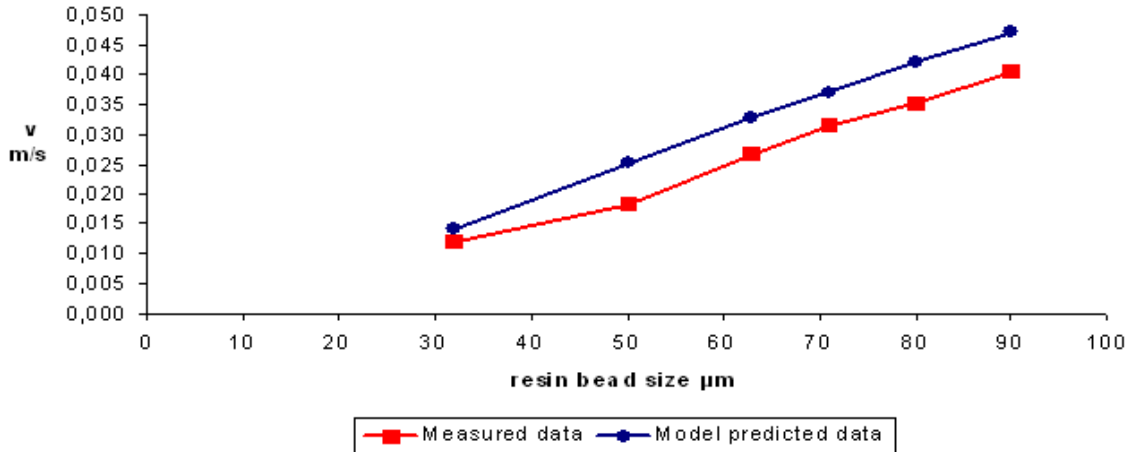


Figure 21 The terminal velocity comparison between measured and model results.

Figure 21 shows the terminal velocity model of Schiller and Naumann results are not fitting with the measured data of each bead size. According to Eq. 13, 14 and 15, the terminal velocity depends very much on the resin density. The resin density will be calibrated in section 4.4.6.

4.4.3 The porosity models of Ergun and Richardson-Zaki

The expanded bed porosity was measured by two methods: firstly is the conversion of Eq.6 (between 20 and 50 cm) and secondly is determined from the conversion of

Eq.16. The conversion equations of both equations are shown below in Eq.21 and Eq.22 respectively.

$$p = 1 - \frac{\Delta P_{20-50}}{\Delta L_{20-50} (\rho_r - \rho_w) g} \quad \text{Eq.21}$$

$$p = 1 - \frac{H_0(1 - p_0)}{H} \quad \text{Eq.22}$$

The both equations are applied in order to check the homogeneousness of expanded resin bed during the fluidization process. It is assumed that if the expanded bed is uniform, the porosity figures, which are calculated from Eq.21 and 22, are equal. The difference between Eq.21 and Eq.22 is the height of bed that is applied in the equation. The porosity of Eq.21 is the expanded porosity between bed heights of 20 cm to 50 cm from the bottom, while Eq.22 is presenting the porosity of whole bed. The comparison of both porosities is also shown in Figure 22. The measurement took place with initial wet resin bed height of 0.63 m. The results of the porosity prediction models of Ergun and Richardson-Zaki, with the input parameters in Table 16, are shown in Table 17 and Figure 22.

Table 16 The parameters for the fluidization models calculation.

Column diameter	0.05	m
Temperature	21.2	°C
Effective bead size	0.00056	m
Resin density	1,681	kg/m ³
Water density	1,000	kg/m ³
Gravity	9.81	m/s ²

Table 17 The measurement porosities and the model porosities.

Velocity m/h	Porosity			
	Eq.21	Eq.22	Ergun	R&Zaki
10.80	0.94	0.61	0.49	0.49
12.32	0.95	0.62	0.52	0.52
14.46	0.95	0.65	0.54	0.56
16.30	0.95	0.67	0.55	0.57
17.83	0.95	0.68	0.57	0.58
18.74	0.96	0.70	0.58	0.59
20.27	0.96	0.71	0.59	0.60
20.88	0.97	0.73	0.60	0.61

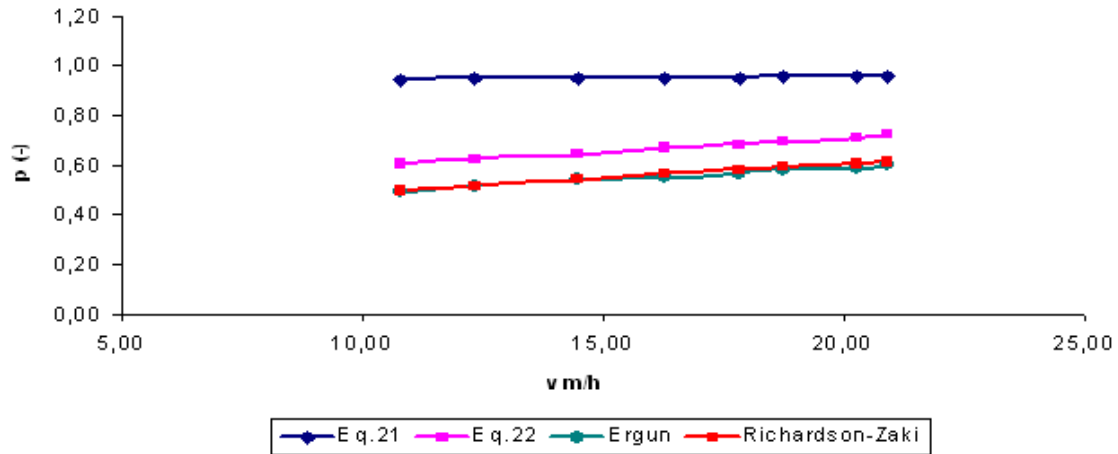


Figure 22 Comparison between the measured porosity and the porosity modelled with Ergun and Richardson-Zaki.

The predicted porosities of both models do not fit with the measured porosity data. The porosities from the Ergun model and from the Richardson-Zaki model have a similar tendency. Comparing the measured data of Eq.21 and Eq.22, it can be seen that the porosity results of these two equations are different (shown in Figure 22). This means that the porosity is not uniform through the whole bed. An increase of feed velocity influences the expanded behaviour of the gel resin. The expanded porosity of the resin is almost linearly increased. Both model results are close to the measured data according to Eq.22, which is a representative of the whole bed. Nevertheless, the Ergun model has an application limit. The empirical model can only be applied when the Reynolds number is between 5 and 100. For this experiment, the Reynolds number is found between 2 and 6. With the WPK drinking water treatment plant conditions treated with the Lewatit VP OC 1071 resin, it is only valid when the feed velocity is 20 m/h or higher. The empirical model of Richardson-Zaki can be applied when the Galileo number is between 21 and 24,000 and the terminal velocity model of Schiller and Naumann requires Galileo number between 3.6 and 10,000. The Galileo number for this experiment is found 1,223. So the model of Richardson-Zaki is valid for whole feed velocity of this experiment.

To find accuracy of the model results, the normalised mean squared error (MSE) is applied (Schagen *et al.*, 2006).

$$MSE = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{H_{measured,i} - H_{predicted}}{H_{measured,i}} \right)^2} \quad \text{Eq.23}$$

By applying all the measurement data and the predicted data from models in Table 16, the MSE can be determined as shown in Table 18.

Table 18 MSE percentages of the models for the porosity prediction.

Ergun		Richardson-Zaki	
Eq.21	Eq.22	Eq.21	Eq.22
41.82	17.19	40.85	15.80

The MSE percentage of both models compared with the measurement data according to Eq.21 and Eq.22 shows that the Richardson-Zaki model is more accurate for the porosity prediction.

4.4.4 The expanded bed height prediction of Ergun and Richardson-Zaki

A comparison between the modelled expanded bed height and the measured data is shown in Figure 23. The modelled expanded bed height is calculated with Eq.16 by using the model porosity data from Table 17, initial resin bed porosity of 0.3303 and initial bed height of 0.63 cm.

The results show that the expanded bed height predicted by the models is lower than the measurement data. The application of the mono-size particle models might be the reason of the prediction error because the Lewatit VP OC 1071 has a high uniformity coefficient (1.80-dry, 1.52-wet).

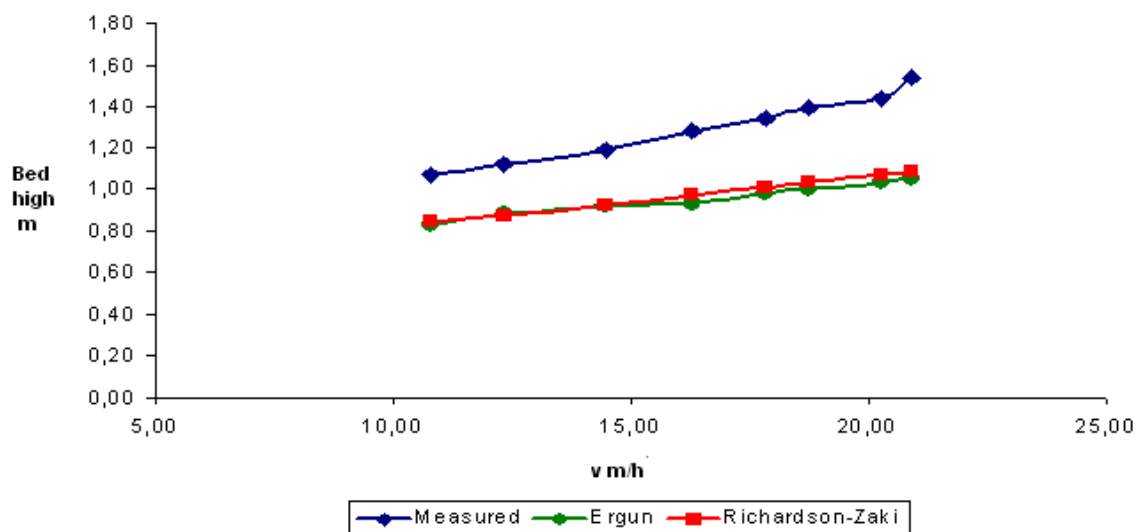


Figure 23 Comparison between the measured bed height and the predicted bed height with models of Ergun and Richardson-Zaki.

To compare the measurement data and the models for the expanded bed height the normalised mean squared error (MSE) is applied. The MSE percentage is determined as shown in Table 19.

Table 19 The MSE percentages of the Models for the expanded bed height prediction.

Ergun	Richardson-Zaki
26.25	24.54

The MSE results show that, the Richardson-Zaki model has more accuracy for the prediction of expanded bed height than Ergun model.

In addition, by applied the dry resin bed porosity instead of wet resin bed porosity in the models, as initial bed porosity, this reason might leads to the calculation error.

Also the wet density is one influenced parameter. To calculate the wet density, the dry porosity is applied under the assumption that the wet porosity is equal to dry porosity. It also can be a reason of the calculation error.

Wet porosity and density of the resin will be calibrated in the following section 4.5.6.

4.4.5 Influence of temperature and feed velocity

According to the model of Ergun and Richardson-Zaki, the temperature and the feed porosity are important parameters for the prediction. Two temperatures of 2 °C and 22 °C and two feed velocities of 20 m/h and 30 m/h are applied into the model. The results of model calculation are shown in Table 20.

Table 20 Influence of temperature and feed velocity.

Temperature(°C)	Expanded porosity			
	Ergun		Richardson-Zaki	
	v = 20m/h	v = 30m/h	v = 20m/h	v = 30m/h
2	0.65	0.72	0.65	0.73
22	0.59	0.66	0.60	0.68

Table 20 shows that the temperature and the feed velocity have an influence on the expansion of the resin bed. By increasing of the temperature, the resin bed is less expanded. The expanded porosity of resin is increased with increase of feed velocity.

4.4.6 Calibration of the wet porosity and density of resin

According to the prediction error, the incorrect value of wet porosity and density might be the cause of an error. When this assumption is true, the calibration of wet porosity and the wet density of resin are required. In order the find, at which wet density and porosity of the gel resin would be fitted with the measured results. The calibration results are shown in Figure 24 and 25. The wet porosity and the wet density are dependent parameters. With the porosity of 0.1338 and the wet density of 1,300 g/l is found that the models results are fitted with the measured data.

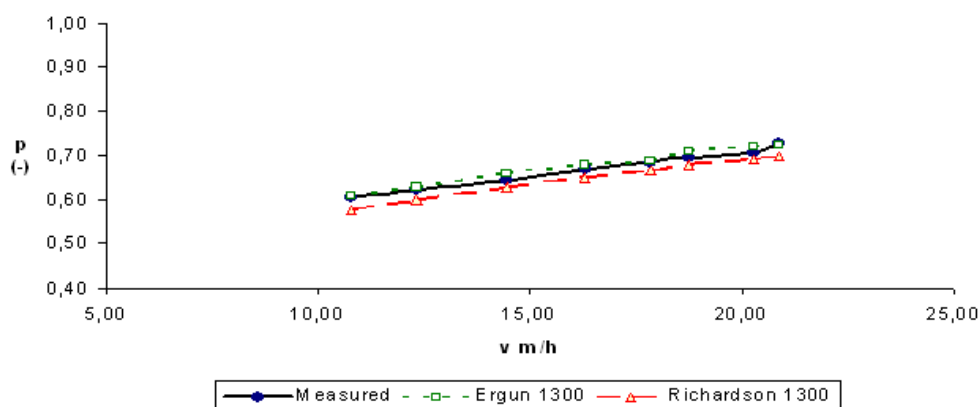


Figure 24 The calibration of wet density for the Ergun model and Richardson-Zaki model.

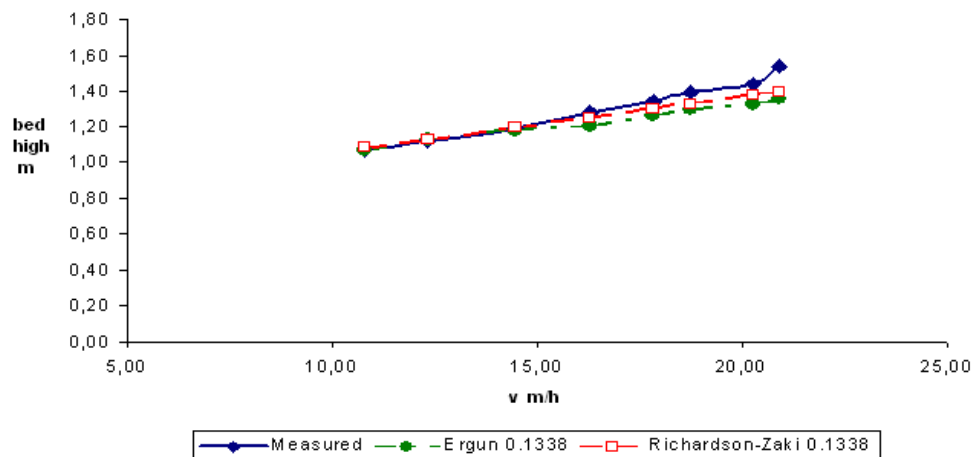


Figure 25 The calibration of wet porosity for the Ergun and Richardson-Zaki model.

In the submerge situation, the resin particles can move freely, and it becomes heavier. With both reasons, the wet resin might be increase and wet porosity might be decrease as the result of the model calibration.

With the calibrated density of 1,300 g/l the Schiller en Naumann model for terminal velocity is recalculated (shown in Figure 26). The prediction error is lower, but still high at about 15% (applied the MSE method)

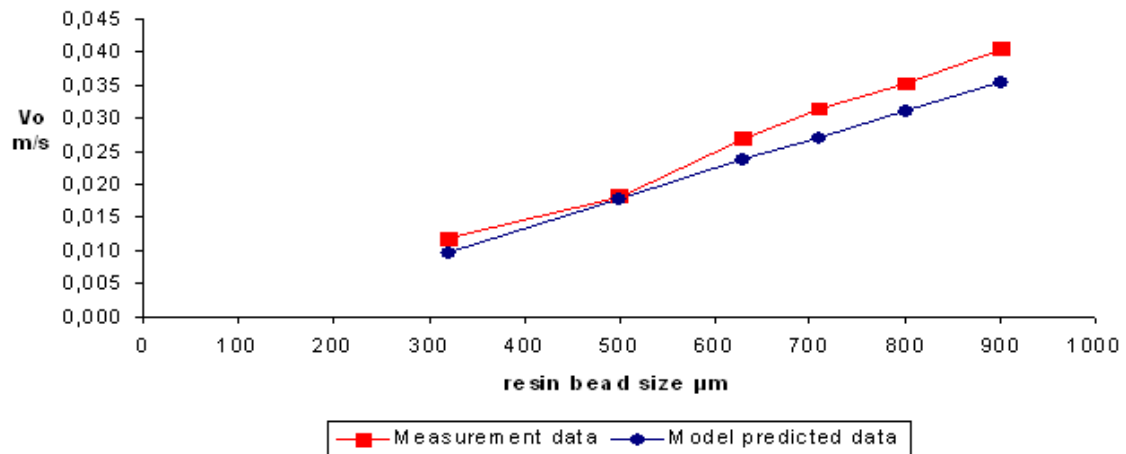


Figure 26 The calibration terminal velocity of Schiller and Naumann model with density of 1,300 g/l.

During further research on the fluidization model for the ion exchange attention has to be giving to the wet resin porosity and density. Also, the models prediction in this thesis is based on the mono-size of resin bead. This might result in the calculation error. The fluidization model for poly-size resin is interesting to test. Because the resin sample is not a mono-size bead, according to the terminal velocity test, the expansion of each size of bead is different. To use only average size or D_{50} might not be sufficient for the prediction.

5 Fluidized ion exchange process design

The design is for WPK water treatment plant. The WPK plant produces one-third of total drinking water production (about 31.3 million m³ per year) for Amsterdam and surrounding areas. It is known that WPK raw water contains a high NOM concentration. NOM is removed with the BAC process with help of ozonation by increasing of biodegradation of NOM. BAC process has a purpose to remove NOM and micro-pollutants and the ozonation has an aim for disinfection. NOM affects the removal efficiency of micro-pollutants and increases the operational costs (BAC filter is faster saturated). The ozone dosing is higher when more NOM is present. The solution to this problem is finding a new treatment process for NOM removal. According to this thesis study, the fluidized ion exchange process is a possibility.

The aim of the fluidized ion exchange process for WPK plant is to reduce the DOC concentration to 3 mg C/l. The fluidized ion exchange process will be placed between rapid sand filtration and the ozonation.

5.1 Design capacity and water quality parameter

The year capacity of WPK plant	31.3	million m ³
Average daily capacity	86,000	m ³

Even through, the WPK treatment plant has a of the clear water reservoir which is function as the buffering for the distribution system, the peak factor in dry years must be taken in to account in order to prevent the water shortage in dry year. The dry year peak factor is 1.08. The day peak factor used is an average of 1.025.(Moel *et al.*,2006)

The design peak factor: (1.08*1.025)	1.11	
The design capacity: (86,000*1.11)/24:	4,000	m ³ /h

For reliability reasons, the number of fluidized ion exchange reactors is designed at 20 reactors. Reactors are separated into 4 groups as shown in Figure 27. The reactor can be shut down for the regeneration process or for maintenance reasons.

Number of reactors:	20	
Flow per reactor: (4,000/20):	200	m ³ /h

The maximum DOC concentration is about 7.2 mg C/l. This figure is confirmed by the DOC analysis result of this thesis. The pH of the raw water is rather constant. The temperature of the water varies largely from about 2 °C in the winter to 22 °C in the summer period. The DOC concentration is rather constant (shown in Figure 28). The temperature change is taking into account because it has influence on the expansion bed behaviour of the resin.

Initial DOC concentration: 7.2 mg C/l
 Expected effluent DOC concentration: 3.0 mg C/l

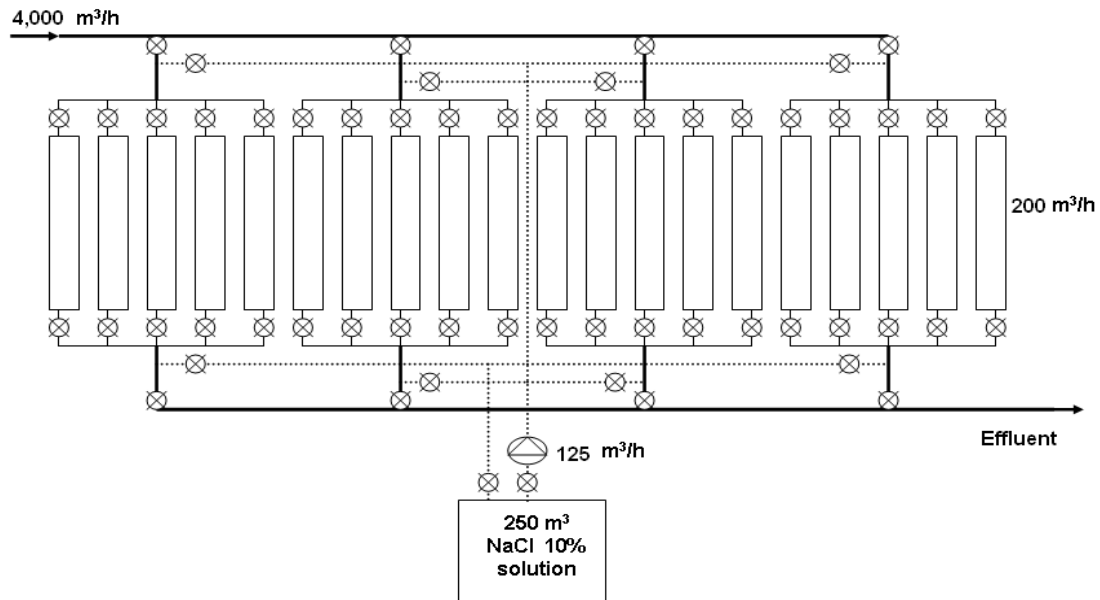


Figure 27 The fluidized ion exchange installation scheme.

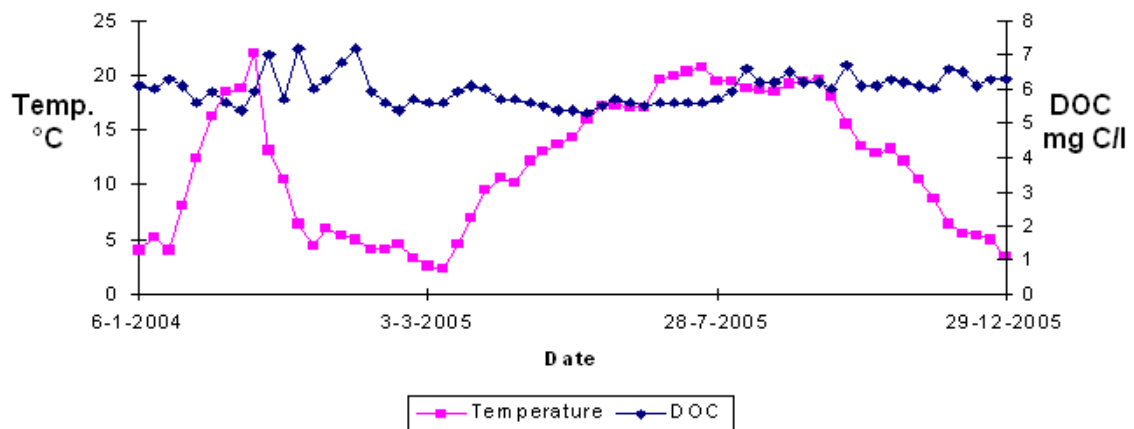


Figure 28 The temperature and DOC concentration data of water after pre-treated during year 2004-2005.

5.2 The fluidized ion exchange reactor

The design is made for a feed velocity of 20 m/h. The surface area of the resin bed is determined.

$$A = \frac{Q}{V} \quad \text{Eq. 24}$$

Surface area: 10.00 m²
 Reactor radius: 1.78 m

Filter bed height: 2.00 m

During the regeneration process, one group of reactors will be shut down. Only 3 groups will be functional (The regeneration process will be described in the section 5.5).

The feed velocity is increased to: $(4,000 \text{ m}^3/\text{h} / (15 \cdot 10 \text{ m}^2)) = 26.7 \text{ m/h}$

When both fluidization model of Ergun and Richardson-Zaki (Eq.10-15) are valid for the expanded bed height prediction (with the calibrated wet density and porosity), the predicted expanded porosity and expanded bed height can be calculated. According to the result of the fluidization experiment, the Richardson-Zaki model is more accurate than Ergun model. Therefore, only the Richardson-Zaki model is applied in this design. The parameters for the model prediction are shown in Table 21 and the model results of expansion bed height are shown in Table 22. In order to calculate the height of expanded bed, the calibrated initial porosity is applied (0.1338).

Table 21 Parameters for the model prediction.

Flow	200	m ³ /h
DOC influence concentration	7.2	mg C/l
Temperature max	22	°C
Temperature min	2	°C
Feed flow velocity (During functional)	20	m/h
Feed flow velocity (During regeneration)	26.7	m/h
Filter bed area	10.00	m ²
Resin bed height	2	m
Resin density	1300	kg/m ³
LDF- k	35.7	h ⁻¹
Freundlich constant K	40.13	g/kg*(m ³ /g) ⁿ
Freundlich constant n	0.87	-

Table 22 Predicted expanded bed porosity and height.

Temperature(celcius)		Richardson-Zaki model prediction			
		Porosity		Bed high	
		v = 20m/h	v = 26.7m/h	v = 20m/h	v = 26.7m/h
Min	2	0.732	0.793	6.46	8.37
Max	22	0.683	0.743	5.46	6.74

The predicted bed heights for this design are 6.46 m and 8.37 m as shown in Table 22 with a feed velocity of 20 m/h and during regeneration process of 26.7 m/h respectively, with the temperature of 2 °C.

In addition, the designed height of reactor has to prevent the resin bead from carrying over.

The reactor height is designed: 9.0 m

5.3 Breakthrough curve prediction

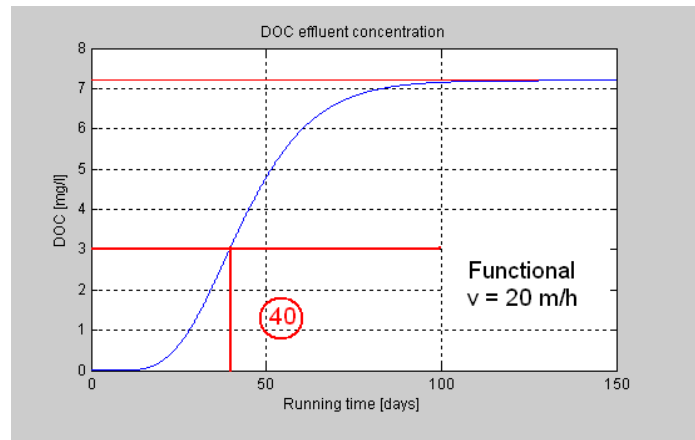


Figure 29 The breakthrough curve of a reactor.

Using the Stimela model, with input parameters from Table 21, for calculating the breakthrough curve of the process, the result is shown in Figure 29. When the maximum effluent DOC concentration is limited at the 3 mg C/l, with the feed velocity of 20 m/h (during the normal functional time), the running time is 40 days.

The running time of the 3 groups of reactors, during one group is regenerated, is also determined and shown in Figure 30.

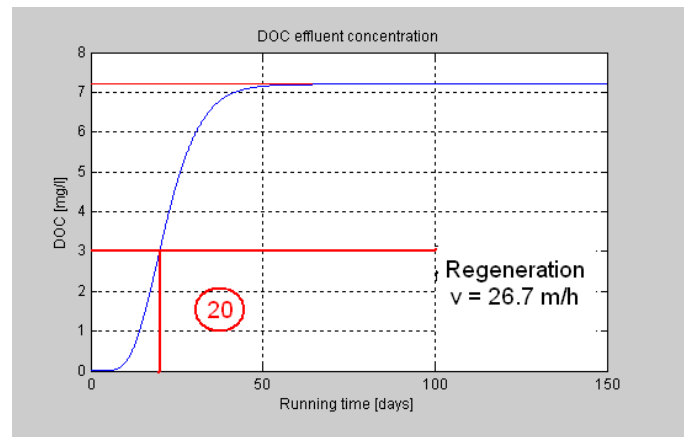


Figure 30 The breakthrough curve of a reactor (15 reactors are functional).

During the regeneration process, one group of reactors is shut down. The feed velocity of the other 3 groups is increased to 26.7 m/h. The running time is found 50% decreased to 20 days. However, the regeneration process takes only a few hours. This treatment situation has almost no effect on the running time of the whole process.

According to Figure 29 and 30, it can also be concluded that the feed velocity has influence on ion exchange process. At low feed velocity, the ion exchange process offers higher NOM exchange efficiency. The running time of the process will also be longer.

5.4 Operation and regeneration process

Fluidized ion exchange reactors consist of 4 groups. Each group has running time of 40 days. It would not be sufficient, if the whole ion exchange process has to shut down for the regeneration of the resin bed.

Because the designed reactors are separated to 4 groups, thus it is not necessary to regenerate all reactors in the same moment. And it would be more cost efficient if one reactor has a longer running time.

When starts each group of reactor with delays of 15 days. According to the breakthrough curve in Figure 29, at 60 days, the average effluent DOC concentration will be only 2.63 mg C/l as shown in Table 23.

Table 23 The running time optimization.

Group 1		Group 2		Group 3		Group 4		Effluent DOC
Time	DOC	Time	DOC	Time	DOC	Time	DOC	
days	Mg C/l	days	mg C/l	days	mg C/l	days	mg C/l	mg C/l
40	3.0	30	1.2	20	0.3	10	0.0	1.13
60	6.0	45	3.5	30	1.0	15	0.0	2.63
80	7.0	60	5.8	40	3.0	20	0.2	4.00
100	7.2	75	6.8	50	4.8	25	0.8	4.90

It means that each reactor can have 60 days of running time or until the DOC concentration reaches 6.0 mg C/l, while total DOC concentration at effluent point is still lower than 3 mg C/l.

The regenerant for the Lewatit VP OC 1071 is recommended to the NaOH concentration of 2-4% or the NaCl concentration of 10% (According to Siegers *et al.*, (2001) the resin maintains an exchange capacity higher than 91% after regeneration with 10% of NaCl solution). The regenerant can be re-used for a few times (depends on the DOC concentrations of raw water). The regeneration process takes place when the effluent DOC concentration reaches the maximum limits of 6 mg C/l at 60 days of running time. The regeneration flow velocity is recommended at maximum 5 m/h with maximum contact time of 30 minutes. With this recommended conditions, the NaCl is estimated at 2,500 kg per regeneration per reactor. After regeneration, the resin has to be rinsed with clean water about 10 bed volumes.

Table 24 The designed reactor and the recommended operating conditions.

Flow	200	m ³ /h	Regeneration days	60	Day
Number of reactor	20	unit	Regenerant	NaCl	-
Filter bed area	10.00	m ²	Concentration	10	%
Filter diameter	3.60	m	Regeneration velocity	5	m/h
Resin bed height	2	m	Minimum contact time	30	minutes
Reactor height	9.00	m	Regenerant volume	2,500	Kg
Resin volume	20	m ³	Rinse water velocity	5	m/h
Flow velocity	20	m/h	Rinse water requirement	10	BV
Contact time	10.65	minutes			

5.5 Cost estimation

The investment cost

The fluidized ion exchange is not yet implemented in the Netherlands. The rough investment cost estimation is calculated based on the softening process where the installation is most similar. According Moel *et al.* (2006), the investment cost factor is between 0.35-0.60 €/m³ yearly capacity. The estimated investment cost of WPK drinking water treatment plant, where the treatment capacity of 31.3 million m³ per year is:

$$\frac{(0.35 + 0.60)}{2} * 31.3 * 10^6 = 14,867,500 \text{ €}$$

The ion exchange process is designed of 10 years depreciation period, which means the investment cost has to divide into 10 years. IN the calculation annually cost, the interest is assumed to be constant at 10%. The cost of treated water per m³ is shown in table 25.

$$Annually = \frac{Investment}{10} * \frac{[1 + r]^n}{[1 + r]^n - 1} \quad \text{Eq.25}$$

Where $r = 10\%$
 $n = 10$

Table 25 The investment cost estimation

Period	10 years
Interest	10%
Cost per year €	2,419,617
Cost per m ³ €	0,08

Operational cost

The operational cost contains all costs which are made during the treatment process. For a fluidized ion exchange, it consists of costs of new resin, regenerant (NaCl), energy, maintenance and administration.

With the assumption that the resin service time is 3 years, the regenerant has to be replaced in every 2 months. The fluidized ion exchange process consumes of 8 Wh/m³. The maintenance costs are estimated of 0.5 % of the investment cost and the administration costs are estimated at 10% of the sum of other operational costs.

The operation cost estimated for WPK drinking water treatment plant is shown in Table 26.

Table 26 The operational cost estimation.

Operational cost	Unit used per year		Cost/Unit (€)	Cost (€)
Resin	97,500	kg	7.00	682,500
Energy	250,400	kWh	0.11	27,544
NaCl	75,000	kg	0.50	37,500
Maintenance				74,338
Adminitration				82,188
Total cost per year				904,070
Total cost per m ³				0.03

To implement the fluidized ion exchange process, the operational cost will be only 3 euro cent increased. In fact, when the DOC concentration is decreased with the fluidized ion exchange process, it can save the operational cost of the ozonation process and the BAC process which might be higher than 3 euro cent. Further, the cost effect of decreasing the DOC concentration by fluidized ion exchange, on the ozonation and the BAC process has to be studied.

Total cost

To implement the ion exchange process at WPK drinking water treatment plant, the total cost is estimated at 11 euro cent per m³ treated water.

6 Conclusions and recommendations

6.1 Conclusions

6.1.1 Batch experiments

1. One aim of this thesis study is to find the most suitable ion exchange resin for WPK drinking water treatment plant. The WPK NOM contains a high DOC concentration of about 7.2 mg C/l with a high degree of humic substances NOM fraction. The WPK NOM can be removed by ion exchange process. From this thesis study can be concluded that the gel resin Lewatit VP OC 1071 is the best resin to use.
2. The MIEX DOC is another good performing ion exchange resin. It removed high amounts of the humic substances and suited for the removal of the building blocks fractions.
3. The sorbent Purolite Macronet 200 is not really efficient for the WPK water. It removed only biopolymers and neutrals fraction while humic substances were not removed.
4. The removal efficiency of weak base Duolite A7 is dependent on the pH. Whenever the pH is low enough for dissociation, the resin can perform as good as a strong base resin and it turns to be a sorbent when the pH is about 8 or higher.
5. To remove the large molecular weight neutrals NOM fraction, the adsorption is a dominant mechanism.

6.1.2 Mathematical modelling of ion exchange

1. MIEX DOC resin can remove NOM faster than other resins. The LDF- k constant of MIEX DOC is also higher than other resins. MIEX DOC has the smallest resin bead size. This can be the reason for the fast removal of NOM.
2. The Freundlich constant K and n describe the exchange capacity of a resin. Increase of K and n values lead to increase of exchange capacity. The Lewatit VP OC 1071 has the highest K and n values and thus the highest exchange capacity.
3. The exchange rate and exchange capacity is a specific property of each resin. With help from the LDF model and Freundlich isotherm the breakthrough curve can be determined. The Lewatit VP OC 1071 showed the longest running time compared with the MIEX DOC and Duolite A7.

6.1.3 Fluidization modelling of ion exchange

1. The Richardson-Zaki model gives more accurate results compared to Ergun model, but both models are not effective for the prediction of the expanded behaviour of gel resin Lewatit VP OC 1071.
2. The wet density and porosity of resin is an important parameter for the model application. Care has to be taken on these two dependent parameters for the model prediction.
3. The temperature and feed velocity have influence on the expansion of the resin bed. By increasing of the temperature the resin bed is less expanded. And the resin bed is more expanded when the feed velocity increases.

6.1.4 Fluidized ion exchange process design

1. Feed velocity has influence on the breakthrough curve. According the results of the Stimela model, the lower feed has shown longer running time before reaching the breakthrough point. By decreased velocity from 30 m/h to 20 m/h, the running time is about 50% increased.
2. At WPK drinking water treatment plant, the DOC concentration needs to be decreased from 7.2 mg C/l to 3.0 mg C/l. This will be done by 20 fluidized ion exchange reactors. The height of reactor is 9 m, the resin bed surface is 10 m², the resin bed height is 2 m and the feed velocity is 20 m/h. The reactors consist of 4 groups, each groups is started with delays of 15 days. With this operational step, the running time of each reactor will be increased from 40 days to 60 days. The operational cost is estimated only 3 euro cent per m³.

6.2 Recommendations

1. More experimental work on specific NOM fractions is needed in order to know more about the kinetic exchange of the NOM fractions. It is interesting to know how the specific NOM fraction is removed in time. In order to explore the kinetic exchange of NOM fraction, the LC-OCD analysis is required more frequently.
2. The effect of NOM change on other processes required to be investigated. When NOM concentration in raw water is decreased before it's transported to the existing treatment process, it might give an effect on the existing processes.
3. The NOM fractions removal in the pilot scale is needed in order to check if the parameters that are obtained from batch experiments are able to apply in full scale. The column test of this thesis is done only to study the fluidized behaviour of ion exchange resin. The NOM removal efficiency of fluidized ion exchange might be less than the prediction result because the resin is a high expandable material.

4. The influence of released ions from the resin (chloride or hydroxyls) on the NOM removal is recommended to study, if the released ions have influence on the exchange process, the linear drive force model and Freundlich isotherm is no further valid for the process mechanism description.
5. The fluidization models that make use of poly-size resin might give better results in the prediction of expansion behaviour. In this thesis, only the mono-size models are tested, this reason might lead to the prediction error.
6. In the regeneration process, the ion exchange resin will released the captured NOM ions into the regenerant. After the process, the regenerant solution will contain a high concentration of NOM. The management and cost has to be further studied.

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Appendix

Symbols for Batch experiments

R1 = the gel resin Lewatit VP OC 1071

R2 = the sorbent Purolite Macronet200

R3 = the weak base resin duolite A7 in raw water pH adjusted to 5

R4 = the weak base resin duolite A7 in normal raw water pH 7.8

R5 = the MIEX DOC

A = Resin kinetics experiment

F = Resin Freundlich isotherm experiment

Appendix 1 Experiment data of UV, DOC and SUVA

The UV absorbance data respect to the Residence time

Samples	Time	UV WaveLength(nm)				Removal %			
	Hour	230	254	280	350				
WPK-0	0.0	0.367	0.212	0.160	0.067				
WPK-1	6.0	0.367	0.212	0.160	0.067				
WPK-2	29.0	0.367	0.211	0.159	0.067				
WPK-3	50.0	0.369	0.213	0.160	0.067				
WPK-4	122.0	0.370	0.214	0.161	0.068				
WPK-5	172.0	0.432	0.219	0.168	0.070				
WPK-6	220.0	0.367	0.213	0.160	0.068				
WPK-7	293.0	0.457	0.218	0.169	0.071				
WPK-8	337.0	0.743	0.233	0.178	0.072				
	0.0	0.367	0.212	0.160	0.067	0.000	0.000	0.000	0.000
R1A-1	6.0	0.321	0.182	0.139	0.064	12.534	14.151	13.125	4.478
R1A-2	29.0	0.220	0.108	0.086	0.050	40.054	48.815	45.912	25.373
R1A-3	50.0	0.203	0.096	0.078	0.045	44.986	54.930	51.250	32.836
R1A-4	122.0	0.176	0.077	0.065	0.042	52.432	64.019	59.627	38.235
R1A-5	172.0	0.225	0.078	0.066	0.042	47.917	64.384	60.714	40.000
R1A-6	220.0	0.172	0.075	0.063	0.041	53.134	64.789	60.625	39.706
R1A-7	293.0	0.246	0.076	0.064	0.042	46.171	65.138	62.130	40.845
R1A-8	337.0	0.499	0.081	0.066	0.042	32.840	65.236	62.921	41.667
	0.0	0.367	0.212	0.160	0.067	0.000	0.000	0.000	0.000
R2A-1	6.0	0.379	0.221	0.166	0.071	-3.270	-4.245	-3.750	-5.970
R2A-2	29.0	0.372	0.215	0.162	0.070	-1.362	-1.896	-1.887	-4.478
R2A-3	50.0	0.356	0.204	0.154	0.065	3.523	4.225	3.750	2.985
R2A-4	122.0	0.350	0.201	0.152	0.065	5.405	6.075	5.590	4.412
R2A-5	172.0	0.409	0.205	0.158	0.067	5.324	6.393	5.952	4.286
R2A-6	220.0	0.348	0.199	0.151	0.065	5.177	6.573	5.625	4.412
R2A-7	293.0	0.435	0.204	0.159	0.068	4.814	6.422	5.917	4.225
R2A-8	337.0	0.721	0.221	0.169	0.069	2.961	5.150	5.056	4.167
	0.0	0.367	0.212	0.160	0.067	0.000	0.000	0.000	0.000
R3A-1	5.0	0.398	0.191	0.147	0.063	7.870	12.785	12.500	10.000
R3A-2	28.0	0.366	0.173	0.133	0.058	15.278	21.005	20.833	17.143
R3A-3	76.0	0.277	0.147	0.113	0.052	24.523	30.986	29.375	23.529
R3A-4	149.0	0.337	0.133	0.105	0.051	26.258	38.991	37.870	28.169
R3A-5	193.0	0.587	0.134	0.103	0.049	20.996	42.489	42.135	31.944
R3A-6	244.0	0.176	0.067	0.045	0.008	52.044	68.396	71.875	88.060
R3A-7									
R3A-8									
	0.0	0.367	0.212	0.160	0.067	0.000	0.000	0.000	0.000
R4A-1	6.0	0.362	0.209	0.157	0.066	1.362	1.415	1.875	1.493
R4A-2	29.0	0.360	0.205	0.155	0.066	1.907	2.844	2.516	1.493
R4A-3	50.0	0.360	0.207	0.155	0.065	2.439	2.817	3.125	2.985
R4A-4	122.0	0.361	0.207	0.151	0.066	2.432	3.271	6.211	2.941
R4A-5	172.0	0.422	0.212	0.162	0.068	2.315	3.196	3.571	2.857
R4A-6	220.0	0.356	0.204	0.153	0.065	2.997	4.225	4.375	4.412
R4A-7	293.0	0.443	0.208	0.161	0.068	3.063	4.587	4.734	4.225
R4A-8	337.0	0.732	0.225	0.171	0.079	1.480	3.433	3.933	-9.722
	0.0	0.367	0.212	0.160	0.067	0.000	0.000	0.000	0.000
R5A-1	6.0	0.230	0.114	0.090	0.048	37.330	46.226	43.750	28.358
R5A-2	29.0	0.202	0.093	0.075	0.043	44.959	55.924	52.830	35.821
R5A-3	50.0	0.202	0.094	0.076	0.043	45.257	55.869	52.500	35.821
R5A-4	122.0	0.201	0.095	0.075	0.044	45.676	55.607	53.416	35.294
R5A-5	172.0	0.252	0.096	0.079	0.045	41.667	56.164	52.976	35.714
R5A-6	220.0	0.198	0.092	0.075	0.043	46.049	56.808	53.125	36.765
R5A-7	293.0	0.275	0.093	0.077	0.044	39.825	57.339	54.438	38.028
R5A-8	337.0	0.538	0.100	0.080	0.044	27.591	57.082	55.056	38.889

The DOC concentration data respect to the Residence time

Time (hour)	WPK	R1A	R2A	R3A(time)	R4A	R5A	WPK
0.0	7.2	7.2	7.2	7.2(0)	7.2	7.2	7.2
6.0	7.1	5.5	6.8	7.0(5)	6.8	4.2	7.1
29.0	7.2	3.5	6.7	6.7(28)	7.1	3.7	7.2
50.0	7.2	4.3	6.9	6.2(76)	7.9	5.0	7.2
122.0	7.4	3.5	7.3	7.17(149)	7.5	4.2	7.4
172.0	8.5	4.2	7.2	4.9(193)	6.2	4.4	8.5
220.0	7.4	3.4	7.2		6.7	4.0	7.4
293.0	7.0	3.3	6.6		6.8	4.2	7.0
337.0	7.1	3.1	6.5		7.2	4.3	7.1

The DOC concentration data respect to the resin dosing

Sample	Resin	Dosing(mg/l)	DOC(mg/l)
R1F-1	Lewatit VP OC 1071	10.80	5.6
R1F-2	Lewatit VP OC 1071	21.30	5.1
R1F-3	Lewatit VP OC 1071	45.10	3.8
R1F-4	Lewatit VP OC 1071	85.30	3.6
R1F-5	Lewatit VP OC 1071	167.60	2.9
R1F-6	Lewatit VP OC 1071	327.40	2.9
R1F-7	Lewatit VP OC 1071	655.10	2.4
R1F-8	Lewatit VP OC 1071	1289.12	2.3
R2F-1	Purolite MN200	13.20	6.5
R2F-2	Purolite MN200	23.60	6.9
R2F-3	Purolite MN200	46.20	6.6
R2F-4	Purolite MN200	81.90	6.5
R2F-5	Purolite MN200	168.90	6.3
R2F-6	Purolite MN200	328.30	6.2
R2F-7	Purolite MN200	656.70	6.3
R2F-8	Purolite MN200	1284.77	6.3
R3F-1	Duolite A7 pH low	11.80	7.0
R3F-2	Duolite A7 pH low	20.30	6.9
R3F-3	Duolite A7 pH low	46.00	6.5
R3F-4	Duolite A7 pH low	86.40	6.1
R3F-5	Duolite A7 pH low	168.80	4.9
R3F-6	Duolite A7 pH low	322.80	4.1
R3F-7	Duolite A7 pH low	644.40	4.7
R3F-8	Duolite A7 pH low	1281.70	3.9
R4F-1	Duolite A7	11.00	7.0
R4F-2	Duolite A7	22.80	6.9
R4F-3	Duolite A7	46.10	6.4
R4F-4	Duolite A7	84.00	6.9
R4F-5	Duolite A7	167.40	7.1
R4F-6	Duolite A7	324.40	7.0
R4F-7	Duolite A7	642.20	7.1
R4F-8	Duolite A7	1288.54	7.4
R5F-1	MIEX	11.30	6.7
R5F-2	MIEX	21.60	6.3
R5F-3	MIEX	44.40	5.7
R5F-4	MIEX	84.60	5.1
R5F-5	MIEX	166.10	3.7
R5F-6	MIEX	322.00	3.6
R5F-7	MIEX	648.30	3.1
R5F-8	MIEX	1283.31	3.1

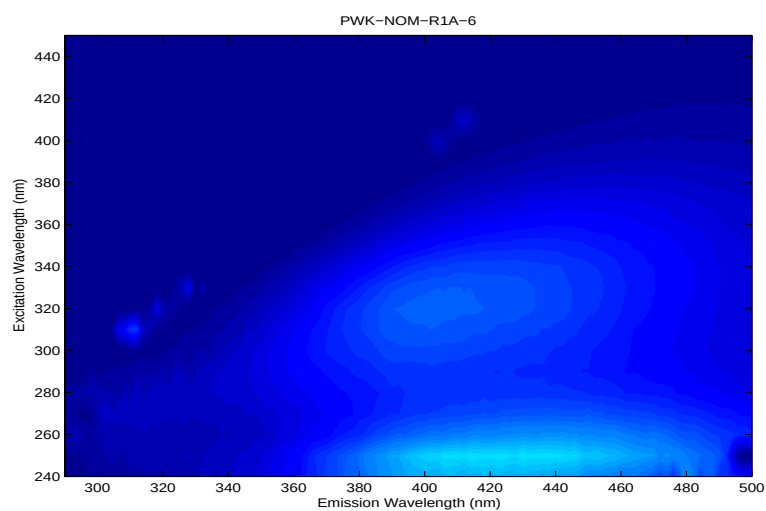
The SUVA value respect of residence time

Sample	Resin	UV(ab/cm)	DOC(mg/l)	SUVA
R1A-1	Lewatit VP OC 1071	0.182	5.5	3.3
R1A-2	Lewatit VP OC 1071	0.108	3.5	3.1
R1A-3	Lewatit VP OC 1071	0.096	4.3	2.2
R1A-4	Lewatit VP OC 1071	0.077	3.5	2.2
R1A-5	Lewatit VP OC 1071	0.078	4.2	1.9
R1A-6	Lewatit VP OC 1071	0.075	3.4	2.2
R1A-7	Lewatit VP OC 1071	0.076	3.3	2.3
R1A-8	Lewatit VP OC 1071	0.081	3.1	2.6
R2A-1	Purolite MN200	0.221	6.8	3.3
R2A-2	Purolite MN200	0.215	6.7	3.2
R2A-3	Purolite MN200	0.204	6.9	3.0
R2A-4	Purolite MN200	0.201	7.3	2.7
R2A-5	Purolite MN200	0.205	7.2	2.8
R2A-6	Purolite MN200	0.199	7.2	2.8
R2A-7	Purolite MN200	0.204	6.6	3.1
R2A-8	Purolite MN200	0.221	6.5	3.4
R3A-1	Duolite A7 pH low	0.191	7	2.7
R3A-2	Duolite A7 pH low	0.173	6.7	2.6
R3A-3	Duolite A7 pH low	0.147	6.2	2.4
R3A-4	Duolite A7 pH low	0.133	7.2	1.9
R3A-5	Duolite A7 pH low	0.134	4.9	2.7
R3A-6	Duolite A7 pH low	0.067		
R3A-7	Duolite A7 pH low			
R3A-8	Duolite A7 pH low			
R4A-1	Duolite A7 pH norm	0.209	6.8	3.1
R4A-2	Duolite A7 pH norm	0.205	7.1	2.9
R4A-3	Duolite A7 pH norm	0.207	7.9	2.6
R4A-4	Duolite A7 pH norm	0.207	7.5	2.8
R4A-5	Duolite A7 pH norm	0.212	6.2	3.4
R4A-6	Duolite A7 pH norm	0.204	6.7	3.0
R4A-7	Duolite A7 pH norm	0.208	6.8	3.1
R4A-8	Duolite A7 pH norm	0.225	7.2	3.1
R5A-1	MIEX	0.114	6.8	1.7
R5A-2	MIEX	0.093	7.1	1.3
R5A-3	MIEX	0.094	7.9	1.2
R5A-4	MIEX	0.095	7.5	1.3
R5A-5	MIEX	0.096	6.2	1.5
R5A-6	MIEX	0.092	6.7	1.4
R5A-7	MIEX	0.093	6.8	1.4
R5A-8	MIEX	0.100	7.2	1.4
WPK-1		0.212	7.1	3.0
WPK-2		0.211	7.2	2.9
WPK-3		0.213	7.2	3.0
WPK-4		0.214	7.4	2.9
WPK-5		0.219	8.5	2.6
WPK-6		0.213	7.4	2.9
WPK-7		0.218	7.0	3.1
WPK-8		0.233	7.1	3.3

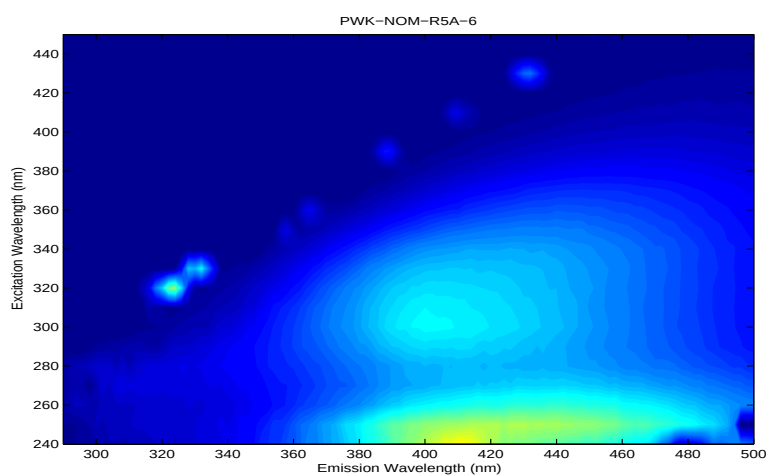
The SUVA calculation with respect to resin dosing

Sample	Resin	Dosing(mg/l)	DOC(mg/l)	UV254nm(ab/cm)	SUVA
R1F-1	Lewatit VP OC 1071	10.80	5.6	0.163	2.9
R1F-2	Lewatit VP OC 1071	21.30	5.1	0.140	2.7
R1F-3	Lewatit VP OC 1071	45.10	3.8	0.104	2.7
R1F-4	Lewatit VP OC 1071	85.30	3.6	0.089	2.5
R1F-5	Lewatit VP OC 1071	167.60	2.9	0.080	2.8
R1F-6	Lewatit VP OC 1071	327.40	2.9	0.073	2.5
R1F-7	Lewatit VP OC 1071	655.10	2.4	0.068	2.8
R1F-8	Lewatit VP OC 1071	1289.12	2.3	0.066	2.9
R2F-1	Purolite MN200	13.20	6.5	0.225	3.5
R2F-2	Purolite MN200	23.60	6.9	0.228	3.3
R2F-3	Purolite MN200	46.20	6.6	0.223	3.4
R2F-4	Purolite MN200	81.90	6.5	0.220	3.4
R2F-5	Purolite MN200	168.90	6.3	0.221	3.5
R2F-6	Purolite MN200	328.30	6.2	0.215	3.5
R2F-7	Purolite MN200	656.70	6.3	0.210	3.3
R2F-8	Purolite MN200	1284.77	6.3	0.207	3.3
R3F-1	Duolite A7 pH low	11.80	7.0	0.153	2.2
R3F-2	Duolite A7 pH low	20.30	6.9	0.145	2.1
R3F-3	Duolite A7 pH low	46.00	6.5	0.123	1.9
R3F-4	Duolite A7 pH low	86.40	6.1	0.106	1.7
R3F-5	Duolite A7 pH low	168.80	4.9	0.069	1.4
R3F-6	Duolite A7 pH low	322.80	4.1	0.048	1.2
R3F-7	Duolite A7 pH low	644.40	4.7	0.039	0.8
R3F-8	Duolite A7 pH low	1281.70	3.9	0.034	0.9
R4F-1	Duolite A7 pH norm	11.00	7.0	0.231	3.3
R4F-2	Duolite A7 pH norm	22.80	6.9	0.228	3.3
R4F-3	Duolite A7 pH norm	46.10	6.4	0.226	3.5
R4F-4	Duolite A7 pH norm	84.00	6.9	0.226	3.3
R4F-5	Duolite A7 pH norm	167.40	7.1	0.224	3.2
R4F-6	Duolite A7 pH norm	324.40	7.0	0.221	3.2
R4F-7	Duolite A7 pH norm	642.20	7.1	0.219	3.1
R4F-8	Duolite A7 pH norm	1288.54	7.4	0.220	3.0
R5F-1	MIEX	11.30	6.7	0.206	3.1
R5F-2	MIEX	21.60	6.3	0.192	3.0
R5F-3	MIEX	44.40	5.7	0.166	2.9
R5F-4	MIEX	84.60	5.1	0.128	2.5
R5F-5	MIEX	166.10	3.7	0.097	2.6
R5F-6	MIEX	322.00	3.6	0.089	2.5
R5F-7	MIEX	648.30	3.1	0.079	2.5
R5F-8	MIEX	1283.31	3.1	0.076	2.5

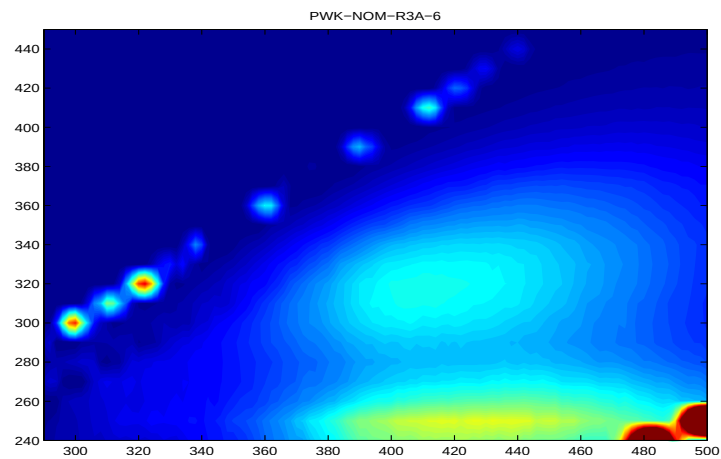
Appendix 2 Fluorescence EEM contour pictures of treated water



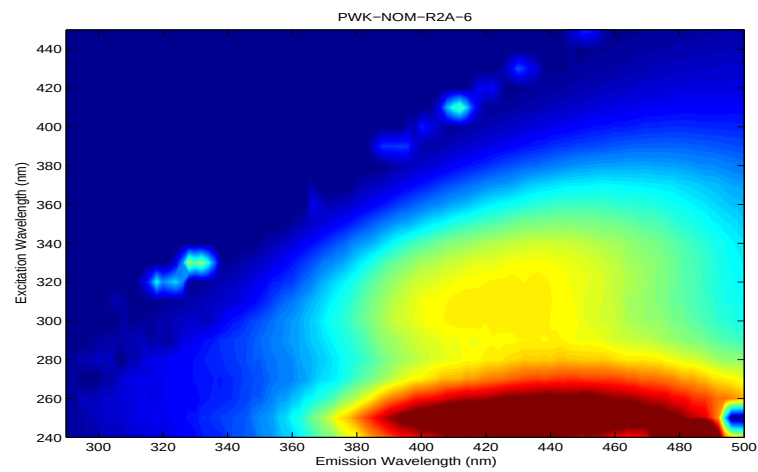
The Fluorescence EEM spectra of treated water with the Lewatit VP OC 1071.



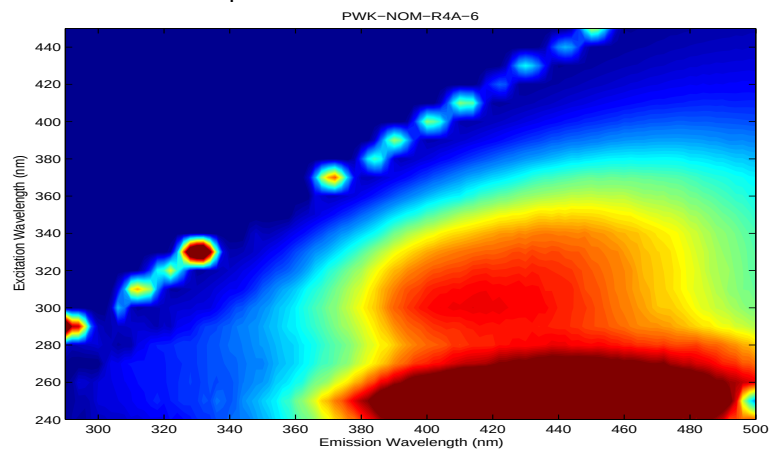
The Fluorescence EEM spectra of treated water with the MIEX.



The Fluorescence EEM spectra of treated water with the Duolite A7 pH 5.

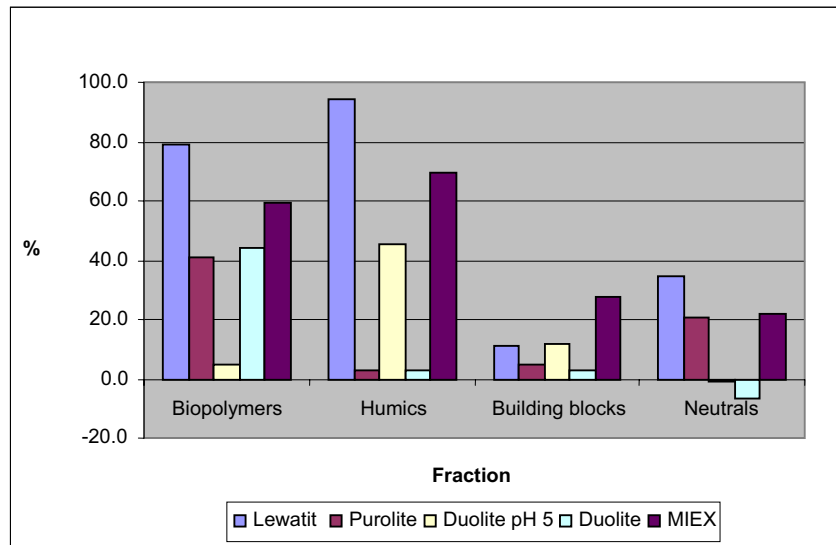


The Fluorescence EEM spectra of treated water with the Purolite Macronet 200.

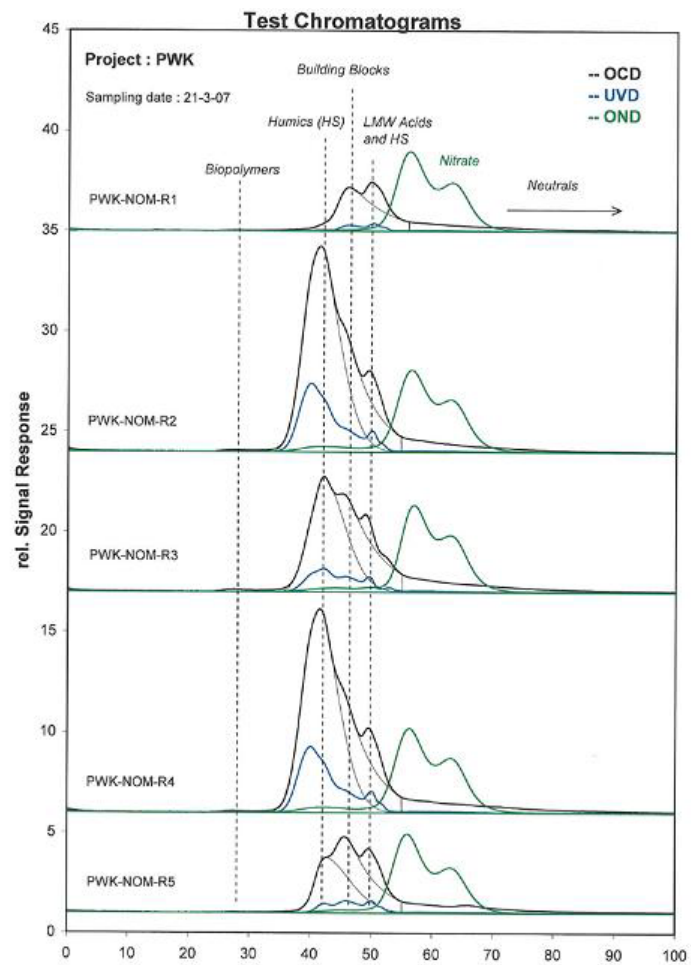


The Fluorescence EEM spectra of treated water with the Duolite A7 pH 7.8.

Appendix 3 Test chromatograms of LC-OCD



The percentage of NOM removal per fraction with respect to different resins.



Appendix 4 Experiment data of hydraulic models of fluidized ion exchange

Data Sieve of analysis

Set	Size(mm)	Mass(g)		Mass(g)	% mass	% Cum
		R&S	Sieve	Resin		
	0	0	0	0	0	0
1	0.32	447.6	396.2	51.4	20.36	0.00
	0.5	509.6	400.6	109	43.19	20.36
	0.63	517.2	482.8	34.4	13.63	63.55
	0.71	468.4	457.7	10.7	4.24	77.18
	0.8	471.4	435.6	35.8	14.18	81.42
	0.9	449.2	438.1	11.1	4.40	95.60
	1.6			252.4		100
2	0.32	451.2	387.7	63.5	26.20	0.00
	0.5	485.2	387	98.2	40.51	26.20
	0.63	503.5	472.4	31.1	12.83	66.71
	0.71	442.4	416.8	25.6	10.56	79.54
	0.8	441.2	434.1	7.1	2.93	90.10
	0.9	453.9	437	16.9	6.97	93.03
	1.6			242.4		100
3	0.32	447.2	383.4	63.8	35.60	0.00
	0.5	449.1	384.1	65	36.27	35.60
	0.63	488	467.1	20.9	11.66	71.88
	0.71	425.2	412.5	12.7	7.09	83.54
	0.8	441.6	431	10.6	5.92	90.63
	0.9	439.4	433.2	6.2	3.46	96.54
	1.6			179.2		100
4	0.32	483.6	383.6	100	29.12	0.00
	0.5	519.8	381.2	138.6	40.36	29.12
	0.63	515.7	466	49.7	14.47	69.48
	0.71	442.4	412.5	29.9	8.71	83.95
	0.8	445.5	430.4	15.1	4.40	92.66
	0.9	442.6	432.5	10.1	2.94	97.06
	1.6			343.4		100
5	0.32	519.1	388.7	127.0	14.82	0.00
	0.5	720.2	383.6	327.7	38.25	14.82
	0.63	668	473.4	189.5	22.11	53.07
	0.71	557.6	411.8	142.0	16.57	75.18
	0.8	493.8	431.2	60.9	7.11	91.75
	0.9	442	432	9.7	1.14	98.86
	1.6			856.8		100

Data of terminal velocity

Size	Terminal velocity (m/s)												
	1	2	3	4	5	6	7	8	9	10	11	12	13
0.32	0.012	0.012	0.012	0.012	0.012	0.013	0.013	0.011	0.011	0.011	0.012	0.011	0.012
0.5	0.018	0.018	0.018	0.019	0.018	0.017	0.017	0.015	0.020	0.024	0.017	0.019	0.018
0.63	0.026	0.026	0.027	0.025	0.026	0.026	0.029	0.025	0.027	0.031	0.029	0.025	0.027
0.71	0.028	0.033	0.029	0.031	0.036	0.029	0.033	0.031	0.033	0.031	0.031	0.029	0.031
0.8	0.037	0.035	0.035	0.034	0.032	0.032	0.033	0.036	0.040	0.033	0.036	0.040	0.035
0.9	0.040	0.039	0.036	0.040	0.033	0.039	0.040	0.044	0.044	0.040	0.050	0.040	0.040

Data of expansion bed experiment

Set 1. Initial bed height 40.5 cm

A = 0.001963 m²
T = 21.2 C
pH = 7.34

Reading	Q M3/h	V m/s	Bed height Cm	Pressure												
				10	20	30	40	50	60	70	80	90	100	110	130	150
0		0	40.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5
10	10	0.00141	58	93.5	92.5	92.2	91.7	91.7	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5
20	14	0.00198	62.5	93.5	92.6	92.2	91.8	91.8	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5
40	22.5	0.00318	72.5	93.5	92.6	92.4	91.9	91.9	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5
58	31	0.00439	84	93.5	92.6	92.4	92	92	91.6	91.5	91.5	91.5	91.5	91.5	91.5	91.5
80	41.5	0.00587	100	93.5	92.6	92.4	92	92	91.8	91.6	91.5	91.6	91.5	91.5	91.5	91.5
90	46	0.00651	108.5	93.5	92.6	92.4	92	92.1	91.8	91.6	91.6	91.3	91.1	91.1	91.2	91.3
95	48.5	0.00686	111	93.5	92.5	92.4	92.1	92.1	91.8	91.5	91.5	91.5	91.2	91.1	91	91.3
100	51	0.00722	118	93.4	92.6	92.4	92.1	92.2	91.6	91.6	91.6	91.5	91.3	91.1	91.1	91.2
120	60.5	0.00856	140	93.4	92.6	92.4	92.1	92.2	91.6	91.6	91.6	91.3	91.1	91.1	91.1	91.1

Set 2. Initial bed height 46.5 cm

$A = 0.001963 \text{ m}^2$

$T = 21.3 \text{ C}$

$\text{pH} = 7.44$

Reading	Q m3/h	V m/s	Bed height Cm	Pressure												
				10	20	30	40	50	60	70	80	90	100	110	130	150
0	0	0.00000	46.5	86	86	86	86	86	86	86	86	86	86	86	86	86
42	10	0.00141	58	88.8	88.2	87.7		87	86.8	86.8	86.8	86.8	86.8	86.8	86.8	86.8
72	15.4	0.00218	64.5	88.8	88.2	87.7		87.2	86.9	86.8	86.8	86.8	86.8	86.8	86.8	86.8
98	20.6	0.00291	71	88.8	88.2	87.8		87.4	87	86.8	86.8	86.8	86.8	86.8	86.8	86.8
150	31	0.00439	84	88.8	88.2	87.8		87.5	87.2	87	86.8	86.8	86.8	86.8	86.8	86.8
185	37.4	0.00529	95	88.8	88.2	87.9		87.6	87.3	87	86.8	86.8	86.8	86.8	86.8	86.8
195	39.2	0.00555	96.5	88.8	88.2	87.9		87.6	87.3	87	86.8	86.8	86.8	86.8	86.8	86.8
205	41	0.00580	102	88.8	88.2	87.9		87.7	87.4	87.2	87	86.8	86.8	86.8	86.8	86.8
210	42	0.00594	137.5	88.8	88.2	87.9		87.7	87.4	87.2	87	87	86.8	86.4	86.5	86.3

Set 3. Initial bed height 52.5 cm

$A = 0.001963 \text{ m}^2$

$T = 20.9 \text{ C}$

$\text{pH} = 7.39$

Reading	Q m3/h	V m/s	Bed height Cm	Pressure												
				10	20	30	40	50	60	70	80	90	100	110	130	150
0	0	0	52	96.6	96.5	96.5	96.5	96.5	94.9	91.2	90.9	87.3	91.5	91.5	91.5	
20	14	0.00198	70	98.3	97.5	97	96.8	96.5	94.9	91.2	90.9	87.2	91	91	91	
40	22.5	0.00318	87.5	98.4	97.7	97	96.9	96.8	94.9	91.2	90.9	87.2	91	91	91	
60	31.5	0.00446	92.8	98.4	97.7	97	96.9	96.9	94.9	91.2	90.9	87.2	91	91	91	
70	36.5	0.00516	106	98.4	97.7	97.1	97	97	94.9	91.2	90.9	87.1	91	91	91	
75	39	0.00552	115	98.4	97.7	97.2	97	97	94.9	91.2	90.9	87.1	91	91	91	
80	41.5	0.00587	123	98.4	97.7	97.2	97	97	94.9	91.2	90.9	87.2	91	91	91	

Set 4. Initial bed height 58.5 cm
 $A = 0.001963 \text{ m}^2$; $T = 21.0 \text{ C}$; $\text{pH} = 7.35$

Reading	Q m3/h	V m/s	Bed height Cm	Pressure													
				10	20	30	40	50	60	70	80	90	100	110	130	150	
0	0	0.00	58														
23	10	0.00141	78.5	93.5	92.5	92.2	91.7	91.7	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5
40	14	0.00198	89.5	93.5	92.6	92.2	91.8	91.8	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5
60	23	0.00325	102.5	93.5	92.6	92.4	91.9	91.9	91.7	91.5	91.5	91.5	91.5	91.5	91.5	91.5	91.5
80	31	0.00439	120	93.5	92.6	92.4	92	92	91.8	91.6	91.5	91.5	91.5	91.5	91.5	91.5	91.5
98	42	0.00594	139	93.5	92.6	92.4	92	92	91.8	91.8	91.6	91.6	91.5	91.5	91.5	91.5	91.5
115	46	0.00651	160	93.5	92.6	92.4	92.1	92.1	91.8	91.8	91.6	91.3	91.1	91.1	91.2	91.3	91.3

Set 5. Initial bed height 63.0 cm
 $A = 0.001963 \text{ m}^2$
 $T = 21.1 \text{ C}$
 $\text{pH} = 7.38$

Reading	Q	V	Bed height	Pressure												
	m3/h	m/s		10	20	30	40	50	60	70	80	90	100	110	130	150
0	0	0	63													
100	21.2	0.00300	107	86.8	86.3	86		85.2	85	84.9	84.7	84.3	84	84		
115	24.2	0.00342	112	87.5	87	86.8		86	85.8	85.5	85.1	85	84.8	84.5		84
135	28.4	0.00402	119	88	87.4	87		86.4	86	85.8	85.5	85.3	85	84.8		84.5
155	32	0.00453	128	88	87.4	87		86.4	86.2	85.9	85.5	85.4	85.1	85	84.8	
170	35	0.00495	134	88	87.4	87		86.4	86.2	85.9	85.7	85.5	85.2	85	84.8	
180	36.8	0.00521	139	88	87.4	87		86.5	86.2	85.9	85.7	85.5	85.2	85	84.8	
198	39.8	0.00563	144	88	87.4	87		86.5	86.2	85.9	85.7	85.5	85.2	85	84.8	
205	41	0.00580	154	88	87.4	87		86.5	86.2	85.9	85.7	85.5	85.2	85	84.8	
207	41.4	0.00586	165	88	87.4	87		86.7	86.2	85.9	85.7	85.5	85.2	85.1	85	84.8
210	42	0.00594	202	88	87.4	87		86.7	86.2	86	85.7	85.6	85.5	85.3	85	85

