Comparison between magnetic ion exchange resin-ultrafiltration and enhanced coagulation–filtration for the treatment of an NOM loaded surface water

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ABSTRACT

The raw water of the waterworks in Kluizen contains high levels of NOM and alkalinity. The current treatment concept comprises enhanced coagulation followed by sludge blanket clarification, filtration, ozonation and Granular Activated Carbon filtration (GAC). A final disinfection with chlorine is applied. The enhanced coagulation, applied to achieve maximum NOM removal, requires a lot of chemicals and produces a lot of solid waste. In spite of this, the treated water still has a relatively high TOC content, resulting in a limited biostability. This disadvantage incited VMW to investigate an alternative treatment scheme consisting of magnetic ion exchange resin, ultrafiltration, ozonation, GAC filtration and chlorine disinfection. The alternative treatment scheme was operated over a two-year period in a pilot plant with a capacity of 50 m$^3$/h, and its results with respect to water quality, chemical demand and operational costs were compared with those of the full-scale plant. The pilot treatment gives rise to an improved removal of NOM, which can be attributed mainly to the magnetic ion exchange resin process. This was shown to have a beneficial effect on both the biostability of the treated water and on the formation of disinfection by-products. The costs associated with the magnetic ion exchange resin process, which can be attributed mainly to resin loss and regeneration, are counterbalanced by cost savings due to lower chemical demand and solid waste formation.

Key words | biostability, magnetic ion exchange resin, NOM removal, THM, Ultrafiltration

INTRODUCTION

The Flemish Water Supply Company (VMW) is operating a 40,000 m$^3$/day waterworks in Kluizen, Belgium, since 1975. The raw water captured during wet winter months from lowlands is stored into reservoirs with a total capacity of 12 Mm$^3$. The most important raw water quality parameters for this study are presented in Table 1. The water is characterised by a high level of TOC or NOM (natural organic matter) in combination with high levels of alkalinity and hardness. During the summer months, algae blooms occur due to the high phosphate content.

Currently, the water is treated by sludge blanket clarification, filtration on hydroanthracite and sand, oxidation with ozone, two-stage Granular Activated Carbon filtration (GAC; contact time two times 15 minutes) and disinfection with chlorine. One of the major goals of the treatment is the removal of NOM, accomplished mainly in the enhanced coagulation and ozonation/GAC filtration steps. The current treatment concept however has some major disadvantages. Firstly, to achieve an acceptable level of NOM removal in the enhanced coagulation step, high doses of chemicals are required: 30 mg/L of sulphuric acid and 11 mg/L of Aluminium are applied, and sodium hydroxide is used to neutralise the water afterwards. This high chemical demand can be attributed to the high pH value and alkalinity of the raw water. The extensive use of chemicals results in a 25% increase of water conductivity.
and the production of large amounts of solid waste, requiring expensive disposal. Secondly, despite the considerable chemical and disposal costs, the residual TOC level of the clear water is still 4.3 mg/L on average, resulting in poor biostability. As a consequence, high chlorine residuals are necessary to prevent microbial growth in the distribution network.

In the near future, VMW wants to upgrade the performance of the thirty-year old Kluizen plant and concurrently increase its production capacity. The development and implementation of a new treatment concept to improve TOC removal is seen as an integral part of the upgrade. The new treatment concept must be cost competitive and more effective in terms of its environmental impact when compared to the existing one. Since 2001, a semi-industrial pilot plant with a capacity of 50 m$^3$/h was operated comprising ultrafiltration, ozonation and two-stage GAC filtration. However, the operation of UF was severely hampered by membrane fouling, shown to be caused by organics-iron complexes. Moreover, the obtained level of TOC removal was unsatisfying. Therefore, in February 2005, a magnetic ion exchange resin DOC treatment unit was added to the pilot plant prior to the UF. The magnetic ion exchange resin process was selected for pilot testing since it has been developed specifically for the removal of NOM from raw water without pretreatment, and because several studies had already demonstrated the positive effects on downstream processes and reductions in THM formation potential and biostability (Drikas et al. 2003; Cromphout et al. 2005a,b; Parsons et al. 2007; Warton et al. 2007). The alternative treatment scheme consisting of magnetic ion exchange resin, UF, ozonation and GAC was operated over a two-year period. In this paper, the results of the pilot treatment with respect to NOM removal are presented and a comparison of the operational costs related to the conventional and the alternative treatment scheme is made.

## METHODS

### 50 m$^3$/h Pilot Plant

**MIEX®**

The MIEX® process was developed by Orica Watercare. (Slunjski et al. 2000). The ion exchange resin is intensively mixed with the raw water in two agitated contactors in series with a contact time of two times 15 minutes. Subsequently, the resin is separated from the water in a settling tank. Most of the settled resin is recycled from the bottom of the separation tank to the contactors, and a small, adjustable amount (5–10%, known as the regeneration rate) is diverted to the regeneration system, where it is stored in a regeneration tank. Once a volume of 400 L of resin has accumulated in the regeneration tank, the resin

| Table 1 | Raw water quality WTP Kluizen |
|---|---|---|---|---|---|
| Parameter | Unit | Average | Stddev | Min | Max |
| Ortho-phosphate | mg/L | 0.28 | 0.25 | 0.0 | 0.9 |
| Conductivity | $\mu$S/cm | 587 | 68 | 423 | 733 |
| Sulfate | $\mu$g/L | 75 | 7.9 | 60 | 93 |
| Chloride | mg/L | 58 | 5.4 | 47 | 82 |
| Suspended Solids | mg/L | 5.5 | 5 | 0 | 23 |
| Chlorophyll | $\mu$g/L | 15 | 15 | 0 | 70 |
| TOC | mg C/L | 11.6 | 4.2 | – | – |
| UV absorption at 254 nm | /m | 30 | 4 | 20 | 38 |
| Color | mg PtCo/L | 32 | 14 | 15 | 90 |
| Total hardness | mmol/L | 2.7 | 0.45 | 1.6 | 3.4 |
| Alkalinity | meq/L | 4.0 | 0.6 | 3.0 | 4.8 |
| Turbidity | NTU | 3.4 | 1.7 | 1.3 | 9.5 |
| pH | – | – | – | 8.0 | 8.6 |
is regenerated by bringing it into contact with 440 L of a 120 g/L NaCl brine. Following the brine drain, the resin is then rinsed with process water to minimise any excess salt within the resin pores, after which the regenerated resin is pumped to a fresh resin tank and from there, it is recycled continuously back to the contactors.

The waste water from the regeneration process (i.e., spent brine and rinsing water) is divided into two fractions. The first fraction, consisting of the portion of spent brine characterised by a high NOM content, is a dark brownish solution that is normally discharged to waste, either directly to sewer, or transported to a waste facility. At Kluizen, liquid waste is not likely to be a viable option, therefore an alternative process was used for producing a solid waste. During this process, the waste water was coagulated using FeCl₃, to remove the organics from the solution, by passing the flocculated suspension through a filter press, thus producing an organic rich filter cake. In a full-scale plant the filtrate from the filter press can be recycled back into the regeneration system. However due to the manual nature of the pilot filter press, it was unfeasible to integrate the recycle stream back into process at the pilot. The second fraction, consisting of the portion of spent brine characterised by a low NOM content, combined with the rinse water, is returned to storage for the production of brine for subsequent regenerations.

**Ultrafiltration**

The dead-end ultrafiltration unit consisted of two independent skids, each equipped with 5 horizontal pressure vessels with a length of 3 m. Each of the vessels contained two membrane modules with a length of 1.5 m, consisting of hollow fiber PES/PVP membranes operated inside-out, with pore sizes around 150 kD. The ultrafiltration unit was operated at a flux of 70 L/m²h; a 40 second backwash was performed every 30 minutes, applying a backwash flux of 250 L/m²h. Dosing of iron or aluminium salts at a concentration of around 3 mg/L into the feed water was performed to control membrane fouling. A chemical backwash alternately with H₂SO₄/H₂O₂ and NaOH/H₂O₂ was performed daily. In May 2006 the UF modules, already in operation since 2001, were replaced by higher permeability modules.

**Ozonation/GAC filtration**

Ozone, produced from oxygen, was mixed with water and subsequently introduced into the main water flow in front of a static mixer. Then the main water flow proceeded directly to the GAC filters. An off-gas ozone destruction system removes non-dissolved gas collected in the upper part of the filters and converts any residual ozone to oxygen. The two GAC pressure filters had a diameter of 2.4 m and contained 12.5 m³ of carbon each. The filters were operated in series, the first one containing exhausted carbon and the second one reactivated carbon. That way, the operation was in correspondence with that of the full scale plant, where GAC is also operated as a two-stage filtration, with the first stage operating between 25,000 and 50,000 bed volumes. After 50,000 bed volumes (two years) the carbon is reactivated and the filter is switched to the second stage position, which operates between 0 and 25,000 bed volumes. The purpose is to achieve NOM removal by biodegradation in the first filtration stage, whereas micropollutants such as pesticides are removed by adsorption in the second stage. This operational mode is based on the observation that NOM removal by GAC filtration can be attributed mainly to adsorption during the first 10,000 bedvolumes and subsequently to biodegradation (e.g., Servais et al. 1994).

**RESULTS AND DISCUSSION**

**NOM removal by magnetic ion exchange resin**

The main operational parameter influencing NOM removal is the effective resin dose (ERD), in units of mL/L, defined as the amount of freshly regenerated resin added to the contactors for each liter of raw water treated. The ERD is obtained by multiplying the average resin concentration in the contactors with the regeneration ratio (i.e., the percentage of the settled resin that is regenerated) (Boyer & Singer 2006). A high resin concentration in the contactors favours the magnetic agglomeration of the resin beads during sedimentation, as such reducing the loss of resin with the effluent. Therefore, the resin concentration was kept constant at a high level of 20–25 mL/L as much as possible in the pilot plant, and the ERD was varied, by changing the regeneration rate. The evolution of TOC removal, decrease
of UV absorbance at 254 nm and the applied ERD during the trial period is shown in Figure 1. The efficiency of the magnetic ion exchange resin treatment with respect to NOM removal clearly decreased during summer periods, despite an increase of the ERD. Analysis of the resin revealed evidence of CaCO₃ scaling on the resin, induced by the high pH value of the raw water occurring in summer time during algae blooms. As a consequence of the scaling, the exchange capacity of the resin decreased from 0.5 to 0.3 eq/L and its apparent density increased from 0.3 to 0.5 kg/L. In July 2006, the resin inventory was treated with hydrochloric acid to remove the CaCO₃ scaling. Since then, the occurrence of further scaling was prevented, by applying a small dose of sulphuric acid to the influent water (5 mg/L). These measures resulted in an improved removal of NOM: 60% of the TOC and 75% of the UV absorbance was removed. At an ERD of 1.5 mL/L (mid November 2006) a slightly higher removal efficiency was observed compared to an ERD of 0.75 mL/L (end of November 2006, February 2007), as shown in Figure 1.

Table 2 presents the average changes in the concentrations of anions and sodium induced by magnetic ion exchange resin treatment of the raw water. The sodium and chloride content of the water increased with 0.13 meq/L due to an incomplete rinsing of the resin after regeneration. Consequently, the amount of exchanged chloride was 0.31 and 0.43 meq/L for the periods without and with acid dosing, respectively. Part of this amount can be attributed to the removal of alkalinity, sulphates and nitrates from the water (see Table 2), the remaining part can be attributed to NOM removal. This results in an estimate of the amount of NOM removed by magnetic ion exchange resin treatment of 0.04 and 0.06 meq/L for the periods without and with acid dosing. The average TOC removal measured during these two periods was equal to 4.41 and 5.69 mg C/L, giving an estimate of the charge density of the NOM of 9 to 11 meq/g C. This value is in accordance with the value of 10 meq/g C reported by Boyer & Singer (2006). The molecular weight of the exchanged humics, obtained from LC-OCD analyses of the influent and effluent (see further) is 617 D. Assuming that the carbon content of humics is 55%, the average valence of an exchanged humic molecule equals 3.4.

The average ERD’s applied during both periods were 1.22 and 1.27 mL/L, respectively, thus on average, 0.25 and 0.34 equivalents were exchanged for each L of freshly regenerated resin added. This means that the greater part of the exchange capacity of the resin was being used, however, a significant amount of it for the unwanted removal of sulphates (60%) and only 14% for NOM removal.

During the period with acid dosing, the average resin loss with the treated effluent was measured to be 5 L/1000 m³. In a full-scale magnetic ion exchange resin plant, much lower resin loss figures are achieved, a guaranteed maximum resin loss value of 2 L/1000 m³ can be provided by the resin supplier.

For every 1,000 m³ of raw water treated, 35–40 kg of filtercake was formed with a dry solids content of 33%. The filtercake contained 60% of organics, 15% of Fe and 15% salt. Unfortunately, its potential use as a soil fertilizer in agriculture is hindered by its high sodium and chloride content. As a consequence, the filtercake will have to be disposed of, with costs related to disposal being equal to 60 Euro/ton.

As mentioned earlier, the filtrate of the filter press was discharged to waste during the pilot trials, whereas on a full-scale plant, it can be reused, considering its low TOC content. Due to the nature and presence of competing anions in the raw water, recycling the filtrate as brine regenerant is likely to affect the efficiency of the exchange processes to some extent. Sulphates, in particular, would gradually accumulate in the regeneration brine until a new equilibrium would be reached. As a result, the resin would be regenerated with a mixture of chloride and sulphate instead of chloride, which may influence the NOM removal efficiency of the magnetic ion exchange resin process.

Figure 1 | Evolution of NOM removal and applied effective resin dose.
The impact of recovering the salt for regeneration is currently subject to further research at Kluizen.

**Ultrafiltration**

The evolution of the permeability (corrected for viscosity of water at 20°C) of the Ultrafiltration membranes during the filtration cycles is shown in Figure 2 for the period after installation of the new UF modules in May 2006.

In literature, fouling due to the presence of NOM has been reported to be a major constraint for the application of Ultrafiltration in surface water (Gray et al. 2004; Makdissi et al. 2004; Katsoufidou et al. 2005) and several studies have shown the effectiveness of in-line coagulation to control this type of fouling (Choi & Dempsey 2004; Holy et al. 2004). During the pilot trials at Kluizen, in-line coagulation with iron or aluminium salts, was found to be necessary to limit the increase of transmembrane pressure during the filtration cycles (Doyen et al. 2003). The applied coagulant dose of around 3 mg Fe/L was determined to achieve some degree of NOM removal, rather than for optimisation of the filtration properties. An average TOC and UV254 absorbance removal of respectively 20% and 25% was obtained under these conditions.

**Ozonation/GAC filtration**

In literature, it was found that magnetic ion exchange resin pretreatment prior to ozonation lowers the ozone consumption and decreases bromate formation. The decrease in bromate formation resulting from magnetic ion exchange resin treatment was related to both a lower ozone demand of the water and to a reduction of the bromide concentration by ion exchange (Clayton & Singer 2004). However, no removal of bromide by magnetic ion exchange resin was observed in the pilot plant at Kluizen (the raw water concentration is 130 mg/L). The ozone consumption of the magnetic ion exchange resin pretreated water was found to be proportional to the ozone dose. On average, 62% of the ozone applied was consumed \( r = 0.57 \) for 18 measurements). In the full scale installation, the average ozone dose equals 2.5 mg/L, of which only 20% (0.5 mg/L) remains after mixing with the main water flow. To obtain the same dissolved ozone concentration in the magnetic ion exchange resin pretreated water, a dose of only 1.3 mg/L is sufficient. Measurements of the bromate concentration after ozonation/GAC filtration as a function of the ozone dose are shown in Figure 3, for both the full scale and the pilot plant. A multiple regression model derived by Sohn.

### Table 2 | Changes in salt and TOC concentrations resulting from magnetic ion exchange resin treatment

<table>
<thead>
<tr>
<th></th>
<th>Period until July 2007</th>
<th>Period from July 2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analysis</td>
<td>51</td>
<td>28</td>
</tr>
<tr>
<td>Alkalinity meq/L</td>
<td>-0.08</td>
<td>-0.1</td>
</tr>
<tr>
<td>Cl(^-) meq/L</td>
<td>+0.44</td>
<td>+0.56</td>
</tr>
<tr>
<td>SO(_4) meq/L</td>
<td>-0.18</td>
<td>-0.26</td>
</tr>
<tr>
<td>Na(^+) meq/L</td>
<td>+0.13</td>
<td>+0.13</td>
</tr>
<tr>
<td>NO(_3) meq/L</td>
<td>-0.015</td>
<td>-0.015</td>
</tr>
<tr>
<td>TOC mg/L</td>
<td>-4.41</td>
<td>-5.69</td>
</tr>
<tr>
<td>Exchanged Cl(^-) meq/L</td>
<td>0.31</td>
<td>0.43</td>
</tr>
<tr>
<td>Cl(^-) exchanged with TOC meq/L</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>TOC charge density meq/g</td>
<td>9</td>
<td>11</td>
</tr>
</tbody>
</table>
et al. (2004) based on data obtained from different plants was applied to interpret these results:

\[
[\text{BrO}_3] = 1.55 \times 10^{-6} \times [\text{TOC}]^{-1.26} \times [\text{pH}]^{5.82} \times [\text{O}_3]^{1.57} \times [\text{Br}]^{0.73} \times t^{0.28} \times (1.035)^{T-20}
\]

With: $[\text{BrO}_3]$: bromate concentration in \(\mu\)g/L.
$[\text{TOC}]$: the TOC concentration in mg C/L.
$[\text{O}_3]$: the applied ozone dose in mg/L.
$[\text{Br}]$: bromide concentration.
$t$: residence time in minutes.
$T$: temperature in °C.

For the same applied dose more bromate is formed in the pilot, due to the lower TOC (4.0 versus 5.1 mg/L) and mainly because of the higher pH (7.8 versus 7.2). For the same ozone residual (0.5 mg/L) the bromate content after magnetic ion exchange resin is the same as after ozonation in the industrial plant (see arrows on the Figure).

**Overall NOM removal**

The TOC content of the water, obtained after the different treatment steps of the pilot plant, is presented in **Figure 4**. As a reference, the TOC content of the clear water resulting from conventional treatment in the full scale plant is also indicated. Three important changes in the operation of the pilot plant are clearly visible in this graph: the connection of the magnetic ion exchange resin unit to the remaining part of the pilot installation in May 2005 and two regenerations of the activated carbon of the second GAC filtration stage, performed in February 2005 and February 2006, after which, the order of the feed to the filters was reversed, as discussed earlier.

Until February 2006, the TOC level after pilot treatment was only slightly lower than the TOC level obtained after full scale conventional treatment. It was only after the introduction of the sulphuric acid dosing in July 2006 to improve NOM removal by magnetic ion exchange resin that the TOC level after pilot treatment became substantially lower than the level after full scale treatment — 2.5 mg C/L versus 4.0 mg C/L in the full scale plant. Similar results were obtained from measurements of the UV absorbance: after pilot treatment UV absorbance was 1.9/m on average, versus 3.8/m after conventional treatment (results not shown).

To determine if a particular fraction of NOM was being removed more preferentially by either of the alternative and the conventional treatment scheme, High Performance Size Exclusion Chromatography (HPSEC) analyses with UV detection were performed at Cranfield University. A typical chromatogram is shown in **Figure 5**. In addition, Liquid Chromatography with Organic Carbon Detection (LC-OCD) analysis was performed in February 2007 at ‘het Waterlaboratorium’ in the Netherlands using DOC-Labor
equipment. The different NOM fractions and their characteristics are presented in Table 3.

The biopolymer fraction in the raw water is low, most of the NOM (72%) consists of humics, with an average molecular weight of 590 D. Eighty percent of these humics were removed by the magnetic ion exchange resin process, and their average molecular weight decreased to 480 D. From these results, the molecular weight of the humic fraction removed by magnetic ion exchange resin can be estimated to be 617 D. The ultrafiltration step only removed an additional 8% of the humics remaining after magnetic ion exchange resin treatment. The combination of magnetic ion exchange resin and ultrafiltration clearly performs a lot better than the conventional coagulation/sedimentation step of the full scale plant, which only removes 50% of the humics.

As expected, ozonation did not change much the TOC level but decreased considerably the UV absorption and thus the aromaticity of the humic substances. The application of ozone did not cause changes in the MW of the humics, or in the hydrophilicity and neither did it result in the formation of acids. The bed-lives of the activated carbon present in the GAC filters were 30,500 and 14,000 bedvolumes for the two GAC filtration stages of the pilot plant and 42,400 and 6,000 bedvolumes for the two stages of the full scale plant. Humics are only removed by adsorption on the carbon (15% after 6,000 BV and 8% after 14,000 BV), whereas the removal of building blocks and neutrals is still important at higher bed-lives and thus by biodegradation (18–22% after 30,500 BV and 14–17% after 42,400 BV). The lower TOC level obtained after pilot treatment is essentially due to a lower humics content, caused by the high removal efficiency of magnetic ion exchange resin with respect to this fraction.

**THM formation**

In the full scale installation, final disinfection of the clear water is performed using chlorine. Because of the high chlorine demand of the clear water, a dose of 2 mg/L of free chlorine has to be added to obtain a residual concentration of 0.25 mg/L in the distribution network, giving rise to an average THM content of 41 µg/L after storage in the clear water reservoir (σ = 10; maximum

Although the THM level is well below the legal standards, VMW wants to decrease it considerably. The chlorine demand of the clear water from the pilot plant is only 0.2 to 0.3 mg/L, which is substantially lower than the chlorine demand of the clear water in the full scale plant. The THM formation potential (THMFP), measured after a contact time of 7 days with 20 mg/L of chlorine, was 277 mg/L after pilot treatment compared to 442 mg/L after conventional treatment.

Biostability

Biostability was measured using the biofilm monitor developed by KIWA (Van der Kooij et al. 1995). This monitor consists of a glass column containing glass rings, which is supplied with the water to be investigated. The formation of biomass on the rings is determined by periodically collecting a ring from the column and measuring the ATP concentration on its surface. The biofilm formation potential (BFP), in units of pg ATP/cm², is defined as the average ATP concentration measured between 100 and 120 days. Two test runs were performed on clear water from the pilot plant, the test periods are indicated on Figure 4. After pilot treatment, almost no biofilm was formed (BFP equal to 70 and 120 pg ATP/cm²), whereas after full-scale treatment (measured on clear water before the final disinfection step), BFP’s of 1152 and 1,533 pg ATP/cm² were observed (Cromphout et al. 2005a, b).

Operating Costs

In the comparison of different treatment schemes, operating costs are an important factor. An overview of the operating costs related to both the conventional full scale treatment scheme and the alternative pilot treatment scheme is presented in Table 4.

- Sulphuric acid is applied for pH correction of the raw water in both treatment schemes. However, prior to conventional flocculation, the dose is 30 mg/L, whereas the dose is limited to 5 mg/L prior to magnetic ion exchange resin treatment. For chemical backwash of the ultrafiltration membranes, another 7 mg/L is required.
- Coagulant is used in the full scale plant at a dose of 11 mg Al/L. In the pilot plant, 3 mg Fe/L was added prior to ultrafiltration and 2 mg Fe/L was used to coagulate the waste water from the magnetic ion exchange resin.
- Sodium hydroxide is applied in both the conventional and the alternative treatment scheme for neutralising the effect of the pH correction with sulphuric acid. In the conventional treatment, 20 mg/L is applied compared to a maximum dose of 6 mg/L in the alternative treatment scheme. Chemical backwash of the ultrafiltration membranes also requires a small dose of NaOH.
- Specific costs associated with the magnetic ion exchange resin process are salt and resin costs.
- Disposal costs for solid waste from conventional flocculation/sedimentation and in-line coagulation are based on removal to the cement industry.

CONCLUSIONS

Compared to conventional clarification-filtration, the combined magnetic ion exchange resin–UF treatment gives rise to an improved removal of NOM, humics in particular, which can be attributed mainly to the magnetic ion exchange resin process. The improved NOM removal was shown to have a beneficial effect on both the biostability of the treated water and its potential for the formation of disinfection by-products. After magnetic ion exchange resin treatment fouling of UF can be limited to an acceptable level if in-line coagulation is applied. The
operating costs associated with the magnetic ion exchange resin process resulting from resin loss and regeneration, are counterbalanced by cost savings due to lower chemical demand and solid waste formation.

REFERENCES


