Applicability of ion exchange for NOM removal from a sulfate-rich surface water incorporating full reuse of the brine

L. Verdickt, W. Closset, V. D’Haeseleer and J. Cromphout

ABSTRACT

The raw water of water treatment works ‘the Blankaart’ (Belgium) is characterized by high levels of NOM (Natural Organic Matter), alkalinity and sulfate. From 2006 until present, the possibility of applying fluidized ion exchange for NOM removal has been investigated at the plant. Pilot testing using Miex® (Magnetic Ion Exchange) resin demonstrated that under standard operating conditions, a TOC (Total Organic Carbon) removal efficiency of 40 to 50% can be achieved. Moreover, jar tests demonstrated that the application of ion exchange as a pretreatment for enhanced coagulation would allow the coagulant dose to be reduced by 60% without compromising effluent quality. Finally, column experiments were conducted to evaluate (i) the effect of full brine reuse and (ii) the possibility of using less expensive conventional ion exchange resins instead of the patented Miex® resin. Recuperation of the waste brine after flocculation with a ferric salt and dewatering was found to have no significant impact on the NOM removal efficiency. Column experiments with Miex® and conventional type 1 anion exchange resins revealed that the fluidization characteristics of both types of resin allow use in fluidized bed systems and that with both types of resin, similar NOM removal efficiencies can be attained. However, higher contact times are required when conventional resins are applied.

Key words | drinking water treatment, natural organic matter, ion exchange

INTRODUCTION

Conventionally, ion exchange for removing NOM (Natural Organic Matter) from drinking water is performed in packed bed reactors, limiting its application in drinking water production to the end of the treatment process. Recently, however, new reactor configurations have been developed in which ion exchange resins are used in suspension, enabling its application to raw surface water. The most widely known example of such a reactor configuration is the patented Miex® DOC (Dissolved Organic Carbon) process, in which an ion exchange resin impregnated with magnetic iron oxide (Miex®) is suspended in a continuously stirred tank reactor and then separated from the treated water in a settler (Slunjski et al. 2002). More recently, attention has shifted towards the application of fluidized bed columns, combining the exchange process and the separation of the resin from the water in one reactor, resulting in a lower footprint (e.g., Cornelissen et al. 2009; Singer et al. 2009). As a result of these developments, the application of ion exchange for NOM removal has received increased attention over the last decade. Many batch and pilot plant studies have been conducted on a variety of raw waters worldwide. In Figure 1, DOC removal efficiencies collected from literature are summarized as a function of the effective resin dose, i.e., the amount of regenerated resin employed per liter of water treated. Although the data presented were mainly obtained from batch and pilot plant studies, results from three full scale Miex® DOC plants, operating at Palm Springs in Florida and Mt Pleasant and Wanneroo in Australia, are included
as well. From Figure 1, it is apparent that maximum DOC removal amounts to 50 to 90%, depending on the raw water quality. To achieve maximum DOC removal, an effective resin dose of 6 mL/L seems to be sufficient for most water sources. With smaller resin doses of 0.5 to 2.5 mL/L, typically applied in full scale plants, a DOC removal efficiency of 25 to 70% can be attained.

In Diksmuide, Belgium, the Flemish Water Supply Company (VMW) operates a surface water treatment plant with a production capacity of 40,000 m$^3$/day named ‘the Blankaart’. The raw water is drawn from the river IJzer and from surrounding lowlands, and is stored in a reservoir with a capacity of 5 Mm$^3$. An overview of the raw water quality is presented in Table 1. The reservoir

![Figure 1](https://iwaponline.com/ws/article-pdf/12/6/878/417043/878.pdf)

**Figure 1** | DOC removal efficiency as a function of effective resin dose. Laboratory-scale results from Singer & Bilyk (2002), Drikas et al. (2003), Fearing et al. (2004), Johnson & Singer (2004), Morran et al. (2004), Boyer & Singer (2005), Humbert et al. (2005), Humbert et al. (2007), Kitis et al. (2007), Mergen et al. (2008), Sani et al. (2008), Apell & Boyer (2010). Pilot scale results from Hammann et al. (2004), Wert et al. (2005), Boyer & Singer (2006), Shorrock & Drage (2006), Singer et al. (2007), Cromphout et al. (2008), Jarvis et al. (2008). Full scale results from Morran et al. (2004), Warton et al. (2007), Hsu & Singer (2009). Note that in all of the studies reported here, the Mieox® resin was used. Humbert et al. (2005, 2007) also performed experiments with conventional resins (RA938, Dowex 11 and Dowex MSA), which are also included in the graph.

### Table 1 | Characteristics of the raw water of the Blankaart reservoir, fed from the river IJzer and from surrounding lowlands

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Average</th>
<th>Stdev</th>
<th>5% percentile</th>
<th>95% percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho-phosphate</td>
<td>mg/L</td>
<td>0.88</td>
<td>0.38</td>
<td>0.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Conductivity</td>
<td>μS/cm</td>
<td>834</td>
<td>46</td>
<td>769</td>
<td>891</td>
</tr>
<tr>
<td>Sulfate</td>
<td>mg/L</td>
<td>100</td>
<td>13</td>
<td>77</td>
<td>120</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/L</td>
<td>96</td>
<td>17</td>
<td>69</td>
<td>126</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/L</td>
<td>17</td>
<td>10</td>
<td>2</td>
<td>34</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>mg/L</td>
<td>3.8</td>
<td>4.4</td>
<td>0</td>
<td>10.8</td>
</tr>
<tr>
<td>DOC</td>
<td>mg C/L</td>
<td>11.1</td>
<td>2.3</td>
<td>9.2</td>
<td>13.9</td>
</tr>
<tr>
<td>UV$_{254}$ absorbance</td>
<td>/m</td>
<td>24.6</td>
<td>3.6</td>
<td>19.5</td>
<td>32.4</td>
</tr>
<tr>
<td>Color</td>
<td>mg PtCo/L</td>
<td>30</td>
<td>8</td>
<td>23</td>
<td>45</td>
</tr>
<tr>
<td>Total hardness</td>
<td>mmol/L</td>
<td>2.8</td>
<td>0.4</td>
<td>2.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>meq/L</td>
<td>3.9</td>
<td>0.6</td>
<td>2.9</td>
<td>4.7</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>3.5</td>
<td>4.0</td>
<td>0.8</td>
<td>11.4</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>7.9</td>
<td></td>
<td></td>
<td>8.8</td>
</tr>
</tbody>
</table>
The raw water is characterized by a high NOM content, with an average TOC (Total Organic Carbon) concentration of 11 mg C/L, combined with a high alkalinity and hardness. The water quality exhibits strong seasonal fluctuations, with the alkalinity and conductivity reaching their highest values in the summer. Moreover, during the summer months, algae blooms occur due to a high phosphate concentration. The current water treatment process consists of trickling filters for biological ammonia oxidation, enhanced coagulation followed by sludge blanket clarification and rapid sand filtration, granular activated carbon filtration, and finally, disinfection with chlorine. One of the main goals of the treatment is the removal of NOM, accomplished mainly in the enhanced coagulation step and to a lesser extent in the activated carbon filters. Due to the high pH and alkalinity of the raw water, high doses of chemicals are required to achieve an acceptable level of NOM removal in the coagulation step. As a result, large amounts of solid waste are produced, requiring expensive disposal. Despite the high chemical and disposal costs, the treated water still has a TOC content of 3.3 mg C/L on average, resulting in poor biostability, a high chlorine demand and the formation of disinfection byproducts. As a result of the disadvantages of the current treatment, VMW investigated the feasibility of applying fluidized ion exchange for NOM removal at the Blankaart plant.

Although the effectiveness of ion exchange for NOM removal has already been demonstrated by numerous studies, a thorough feasibility study was considered necessary due to several reasons:

- The raw water of the Blankaart reservoir is characterized by a high sulfate concentration (100 mg/L on average), and it was anticipated that a large part of the exchange capacity of the resin would go to sulfate removal instead of NOM removal.
- Application of ion exchange results in a waste stream highly loaded with salts and NOM, which has to be discharged. However, at the Blankaart plant, discharge of liquid waste streams is undesirable. Hence, the feasibility of complete brine reuse was investigated.
- Most of the results available in the literature were obtained from jar tests or studies using the patented Miex® DOC process, whereas at the Blankaart, the application of a fluidized bed system is under consideration.
- The major operational cost of ion exchange in fluidized bed is attributable to the replacement of resin that is carried over from the reactor with the effluent. Therefore, the possibility to apply less expensive conventional anion exchange resins instead of Miex® was addressed.

In a first stage, single contact laboratory experiments were conducted to assess the NOM removal efficiency of ion exchange, applied directly on the raw reservoir water. Additionally, lab scale coagulation tests were conducted to get an idea of the impact of ion exchange pretreatment on the coagulant dose. In a second stage, a pilot plant was operated for a year-round period to assess full scale operation of a fluidized bed system. In parallel with the pilot tests, a test column was used to (i) investigate the feasibility of complete brine reuse and (ii) evaluate the possibility of applying conventional ion exchange resins instead of Miex® in fluidized bed columns. In this paper, the main results of the feasibility study are elaborated.

MATERIALS AND METHODS

Jar tests

Ion exchange

The raw water was contacted with Miex® resin taken from the contactor of a Miex® DOC pilot plant operated at another VMW water treatment works (Cromphout et al. 2008). By applying the resin at a concentration of 25 mL/L, an effective resin dose of 2.5 mL/L was obtained, as the Klui-zen plant was operated at a regeneration ratio of 10%. A 20 min contact time was observed and subsequently, the supernatant was withdrawn for use in coagulation tests. Before and after Miex® treatment, chemical oxygen demand (KMnO4), UV254 absorbance and turbidity were measured. Note that prior to the ion exchange experiments, the pH of the raw water was lowered to 7.6–7.8 to avoid precipitation of CaCO3 on the resin beads, as this was shown to decrease the exchange capacity of the resin (Cromphout et al. 2008).
Coagulation

Jar tests were performed

- on the raw water, acidified with 80 mg H₂SO₄/L, the sulfuric acid dose used for pH conditioning at the full scale plant;
- on the effluent of the Miex® jar tests.

The water was coagulated with doses of 0, 4, 8, 12, 16 and 20 mg Fe/L in 1 L jars under rapid mixing, followed by slow mixing during 10 min. Subsequently, the flocs were separated from the water by flotation or sedimentation. In the case of flotation, 0.1 L of oversaturated water was added, and a flotation time of 5 min was observed. In the case of sedimentation, a sedimentation time of 30 min was observed. Before and after treatment, chemical oxygen demand (KMnO₄), UV₂₅₄ absorbance and turbidity were measured. After treatment, residual iron was measured as well.

Pilot plant

A fluidized bed plant with a treatment capacity of 1.25 m³/h was provided by Orica Watercare, the manufacturer of the Miex® resin. The plant was operated at the Blankaar from June 2008 until July 2009. In Figure 2, a process scheme of the pilot plant is presented. The raw water was contacted with the Miex® resin in an upflow reactor, equipped with lamellae separators at the top to separate the resin from the effluent. Loaded resin was continuously withdrawn from the contactor at a low flow rate and transferred to the regeneration system, where it was regenerated with a 10% NaCl solution. Regenerated resin was continuously pumped from the regeneration system back to the contactor.

Throughout the trial period, the effective resin dose was kept constant at 1.0 mL/L. In other words, 1,000 bed volumes of raw water were treated per bed volume of resin regenerated. Twice a week, raw water and effluent samples were collected and monitored for TOC, UV₂₅₄ absorbance, pH, turbidity, conductivity, chloride, sulfate, nitrate, alkalinity and sodium.

Ion exchange column

A fluidized bed column with a nominal treatment capacity of 150 L/h was operated from 2008 until 2010, with in situ regeneration of the resin every 1,500 bed volumes of raw water treated. A schematic view of the column is given in Figure 3. Throughout each column experiment, the effluent was sampled after 60, 100, 200, 300, 600, 900, 1,200 and 1,500 bed volumes and monitored for TOC, UV₂₅₄ absorbance, pH, turbidity, conductivity, chloride, sulfate, nitrate,
alkalinity and sodium. Overall removal efficiencies that would be obtained when operating a continuous fluidized bed system at 400, 1,000 and 1,500 bed volumes were calculated by linear interpolation from removal efficiencies measured throughout the experiment.

To assess the possibility of complete brine reuse, the waste brine from each operating cycle was flocculated with ferric chloride and subsequently filter pressed, and the filtrate was reused as brine in the following cycle. To maintain the brine pH and conductivity at a constant level (pH 7 and conductivity 140 mS/cm), NaOH and NaCl were added to the filtrate prior to its reuse. As a reference, column experiments were conducted using a 10% w/w solution of NaCl for regeneration, applying a dose of 1.84 eq Cl⁻ per L of resin.

To evaluate the use of less expensive resins instead of the patented Miex®, experiments were conducted with two conventional type 1 anion exchange resins with a polyacrylic matrix and a macroporous structure (Purolite A860S and Lewatit VPOC 1071). Some important features of the resins used are brought together in Table 2. For each resin, the fluidization of the resin bed was measured as a function of the upward flow velocity at 4 and 16–20 °C. The importance of the exchange kinetics for each of the resins was assessed by operating the column at different upward flow rates, resulting in empty bed contact times of 37, 60 and 120 s.

### Table 2 | Overview of the resins used in the column experiments

<table>
<thead>
<tr>
<th>Resin</th>
<th>Functionality</th>
<th>Matrix</th>
<th>Structure</th>
<th>Water content (%)</th>
<th>Bead size (μm)</th>
<th>Exchange capacity (meq/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewatit VPOC 1071</td>
<td>Type I</td>
<td>Acryl</td>
<td>Gel</td>
<td>55–61</td>
<td>550 ± 50</td>
<td>1.25</td>
</tr>
<tr>
<td>Miex®</td>
<td>Type I</td>
<td>Acryl</td>
<td>Macroporous</td>
<td>65</td>
<td>150–180</td>
<td>0.52</td>
</tr>
<tr>
<td>Purolite A860S</td>
<td>Type I</td>
<td>Acryl</td>
<td>Macroporous</td>
<td>66–72</td>
<td>425–1,200</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Figure 3 | Schematic view and picture of the ion exchange column (internal diameter = 0.1 m, resin volume = 2 L). The equipment for in situ regeneration is labeled in italic.
RESULTS

Preliminary jar tests

An average removal efficiency of 32% for chemical oxygen demand (KMnO₄) was obtained when an effective resin dose of 2.5 mL/L was applied. The UV₂₅₄ absorbance of the water was reduced by 55%. These results were somewhat poorer than expected from the pilot trial at the Kluizen plant mentioned above, where a TOC removal efficiency of 60% was achieved on similar raw water by operating the Miex® DOC process at an effective resin dose of 0.75 to 1.5 mL/L (Cromphout et al. 2008). Nevertheless, it was found that incorporating Miex® treatment ahead of the conventional treatment train at the Blankaart would allow the ferric dose to be reduced from 20 to 8 mg Fe/L without compromising the final water quality, as can be seen from Figure 4. This observation is in accordance with literature, where reductions of the required coagulant dose by 50 to 80% have been reported by Singer & Bilyk (2002), Fearing et al. (2004), Morrán et al. (2004), Boyer & Singer (2005, 2006), Humbert et al. (2005, 2007), Drikas et al. (2003, 2011) and Mergen et al. (2008). Kitis et al. (2007) mentioned somewhat smaller reductions of 25 to 50%.

Pilot results

NOM removal

The pilot plant findings with respect to NOM removal are presented in Figure 5. Applying an effective resin dose of 1 mL/L resulted in a 40 to 50% removal of TOC and a 60%
to 70% reduction of UV254 absorbance. The lowest removal efficiency for NOM was observed during early summer, when the specific UV254 absorbance of the raw water was at its lowest. When compared to the literature results collected in Figure 1, it is apparent that the results obtained at the Blankaart are situated around the average. Moreover, the observed NOM removal is higher than the one obtained in the preliminary batch experiments, despite the fact that in the pilot trial, a lower effective resin dose was applied (1.0 versus 2.5 mL/L). A possible explanation for this discrepancy is that the resin that was used in the batch experiments was taken from the contactor of a Miex® DOC pilot plant which had been out of operation for several months.

Removal of competing anions

Table 3 provides an overview of the average changes in UV254 absorbance and in the concentrations of the most important inorganic anions, TOC, and sodium, measured before and after pilot plant treatment. Both the sodium and the chloride content of the water increased with 0.12 meq/L due to incomplete rinsing of the resin after regeneration, leaving 0.28 meq/L of the total increase of the chloride concentration to be attributable to ion exchange. However, the major part of this amount can be attributed to the removal of sulfate (0.19 meq/L), and a smaller part to the removal of bicarbonate (0.05 meq/L) and nitrate (0.01 meq/L), leaving only 0.03 meq/L of chloride that was effectively exchanged for NOM. The amount of TOC removed was measured to be 3.96 mg C/L, so the charge density of the organic matter can be estimated to be around 8 meq/g C. This value is in good agreement with the values of 9 to 11 and 10 meq/g C reported by Cromphout et al. (2008) and Boyer & Singer (2006), respectively.

As anticipated, a major part of the practical exchange capacity of the resin goes to the removal of sulfate (68%), whereas only 11% is used effectively for TOC removal. Similar results were obtained at the Kluizen water treatment works, where 14% of the total amount of chloride exchanged could be attributed to NOM removal, and 60% to sulfate removal (Cromphout et al. 2008). Shorrock & Drage (2006), on the contrary, observed no significant sulfate removal when the Miex® DOC process was applied at an effective resin dose of 0.8 mL/L on raw water with a sulfate content of 120 mg/L. A study addressing the actual impact of sulfate on NOM removal was performed by Boyer & Singer (2006). They augmented the sulfate content of low conductivity water from less than 10 mg/L to 50 mg/L, and found that as a result, the TOC removal efficiency of the Miex® DOC process decreased from around 70% to 51%. Moreover, in pilot trials performed on four different surface waters, the poorest TOC removal was observed for raw water containing 230 to 250 mg sulfate/L (Singer et al. 2007).

Column experiments

Brine recuperation

Estimates of the overall removal efficiency that would be obtained for NOM, sulfate, nitrate and alkalinity when operating a full scale fluidized bed system at 400, 1,000 and 1,500 bed volumes were calculated by linear interpolation from the effluent concentrations measured throughout the experiments. Figure 6 presents results for Miex® regenerated with NaCl on the one hand and for Miex® applying brine reuse on the other hand. The feasibility of brine reuse was evaluated by performing a series of 14 column experiments where the waste brine of each experiment was reused in the next one after flocculation and filter pressing. In Figure 6(b), average results from the last five experiments of the series are reported.

When NaCl is used for regeneration and the fluidized bed system is operated at 400 bed volumes, substantial removal of sulfate, nitrate and alkalinity takes place. The removal of inorganics decreases drastically when the amount of bed...
volumes is increased from 400 to 1,000 and further to 1,500. Note that the estimates of the overall removal efficiencies for NOM, sulfate, nitrate and alkalinity obtained for 1,000 bed volumes are in excellent accordance with the results from the pilot trial applying an effective resin dose of 1 mL/L (see Table 3), indicating that the results obtained from the test column are easily transferable to a large scale.

Recuperation of the brine, resulting in the accumulation of sulfates in the brine, gave rise to a decrease of the unnecessary removal of sulfates, nitrates and alkalinity, without significantly influencing NOM removal. Moreover, the salt consumption was reduced by a factor of four. On average, 26 g NaCl was required per L of brine to keep the brine conductivity at a constant level, whereas a 10% NaCl solution contains 107 g NaCl/L. In addition, 6 g FeCl₃/L was required to flocculate the brine and 0.3 g NaOH/L to restore the pH to neutral after filter pressing.

Use of conventional anion exchange resins

The results presented above were all obtained using the patented Miex® resin. In addition, column experiments were conducted using two conventional ion exchange resins (Purolite A860S and Lewatit VPOC 1071) instead of the more expensive Miex® resin. Similar NOM removal efficiencies were obtained with all three of the resins. However, whereas for Miex®, a contact time of about 40 s suffices to achieve maximum NOM removal, this was not the case for the conventional resins, characterized by a much larger bead size. The impact that increasing the contact time from 40 s to 1 min and further...
to 2 min has on the NOM removal efficiency is illustrated for Purolite A860S in Figure 7. As can be seen from the graph, both the reduction of UV<sub>254</sub> absorbance and the removal efficiency for TOC increase considerably when the contact time is increased. Obviously, these results do not come as a surprise, as kinetic experiments by other authors already demonstrated the importance of bead size with respect to exchange kinetics (e.g., Humbert et al. 2005, 2007; Cornelissen et al. 2008). The fluidization characteristics of Miex<sup>®</sup>, Purolite A860S and Lewatit VPOC 1071 are presented in Figure 8. From the results, it is clear that both Miex<sup>®</sup> and the conventional resins can be used in fluidized bed systems operated at a surface loading of 15 to 25 m/h.

**CONCLUSIONS**

The feasibility study demonstrated that a TOC removal efficiency of 40 to 50% is achievable by applying ion exchange directly on the raw water of the Blankoart reservoir, despite its high sulfate content. Moreover, recuperation of the waste brine by means of flocculation and dewatering was shown not to affect NOM removal. Hence, it will be possible to run the ion exchange process without producing liquid waste streams. Based on the pilot tests and assuming the resin loss to be 2 mL/m<sup>2</sup>, the operational cost of applying Miex<sup>®</sup> in a fluidized bed system, incorporating full reuse of the brine, was estimated to be 3.6 €/t/m<sup>3</sup>. Despite the low resin loss that was assumed, the operational cost was found to be mainly attributable to this loss. Hence, replacing Miex<sup>®</sup> by a conventional resin is a valuable option, bearing in mind that conventional resins are approximately eight times less expensive than Miex<sup>®</sup>.

Before the application of ion exchange on a full scale may be considered, some remaining questions need to be answered. Therefore, a 40 m<sup>3</sup>/h pilot plant is currently under construction. Further research will first of all focus on the resin loss, as this represents the main operational cost of the ion exchange process. The resin loss observed in the pilot tests and the column experiments has not been reported as it was not considered to be representative of the resin loss at a full scale plant. Nevertheless, as the resin loss seemed to increase significantly during algae blooms, the impact of algae bloom on the ion exchange process will be examined closely. In addition, the 40 m<sup>3</sup>/h pilot plant will be used to evaluate the brine reuse procedure and the applicability of conventional resins on a large scale. Finally, it is important to build up some experience with operating a large scale fluidized bed installation in view of the design of a full scale plant with a capacity of 2,000 m<sup>3</sup>/h.

**REFERENCES**


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[Links and references as needed]