Magnetic ion exchange resin treatment for drinking water production

B. Sani, E. Basile, L. Rossi and C. Lubello

ABSTRACT

Italian drinking water treatment plants (DWTP) generally use chlorine-based chemicals to achieve the oxidation/disinfection phases of their treatment trains. The main problem related to the application of such disinfectants consists in the formation of disinfection by-products (DBPs) as a result of the reaction with organic substances in the water. Italian regulations set very strict limits for the maximum concentration of chlorine DBPs and, for many DWTPs, the compliance with such a regulation is difficult. Non-oxidative pre-treatments, able to remove organic substances from the water prior to chlorination, could be a suitable solution to overcome this problem. These treatments could increase the water quality, decrease the oxidant demand and, hence, reduce the formation of DBPs. This paper presents an experimental investigation of ion exchange processes for the dissolved organic carbon (DOC) removal by using MIEX® resin. The process was studied as a pre-treatment on raw river water. The DOC removal efficiency and the effects on downstream processes of the treatment train were evaluated.

Key words | clariflocculation, DBPs, DOC, ion exchange, MIEX®

INTRODUCTION

Natural organic matter (NOM) concentration is one of the most important parameters for the evaluation of drinking water quality. Organic substances have to be removed from drinking water because they could produce odour and colour problems, could be responsible for microbial re-growth in the distribution network and could lead to the formation of harmful DBPs (Bull & Kopfler 1991; Nikolaou et al. 1999).

Chemical disinfectants traditionally applied in drinking water treatment plants (DWTPs) are chlorine (Cl₂), hypochlorites (NaClO, Ca(ClO)₂) and chlorine dioxide (ClO₂). Chlorine and hypochlorites react with dissolved organic substances to form trihalomethanes (THMs), whereas chlorine dioxide leads to the formation of chlorite (ClO₂⁻) and chlorate ions.

Italian regulations set very strict limits for the maximum concentration of chlorine DBPs: 30 µg/L for THMs and 700 µg/L for ClO₂⁻. Moreover a minimum concentration of 0.2 mg/L of residual chlorine is recommended as a warranty of the disinfection efficiency. For many Italian plants the compliance with such regulations is very difficult to achieve, in particular for the DWTPs that treat raw river water and for those that feed wide distribution networks where a high dosage of chlorine is needed in order to maintain the minimum residual chlorine concentration.

Non-oxidative pre-treatments, able to remove organic substances from the water prior to chlorination, could be a suitable solution to overcome this problem.

The main components of DOC (Dissolved Organic Carbon), such as humic and fulvic acids, ionize at a pH between 6 and 8, the typical range for natural waters (Slunjski et al. 1999). In the ionized form, dissolved organic substances can be removed by ion exchange treatment, in particular by the application of anionic resins.

Ion exchange resins are composed of a three-dimensional structure of styrenic (or acrylic) polymeric chains...
with divinylbenzene crosslinkings. Electrically charged functional groups are placed on the polymeric chains and differently charged ions (counter-ions) are linked to the functional groups by electrostatic forces. When the ion exchange resin is applied to water, the ions in the water are exchanged with the counter-ions on the resin.

This paper presents an experimental investigation using a magnetic ion exchange resin (MIEX® resin), produced by Orica Watercare. The MIEX® resin is an SBA (Strong Base Anion) resin type 1, in its chloride form, and it is composed of a macroporous structure, polyacrylic matrix with a dispersed magnetic component. The DOC\(^-\) removal is achieved by the exchange with Cl\(^-\) (Figure 1).

The MIEX® process can be divided into three main phases (Figure 2): ion exchange, resin separation from the treated water and regeneration. The ion exchange reaction between DOC\(^-\) and Cl\(^-\) is carried out in a completely mixed reactor.

At the end of the contact time of the reaction, the resin is separated from the treated water in a settler, where the settling is enhanced because large agglomerates of resin are formed through the magnetic action. The settled resin is then re-circulated into the reactor and a small amount (5–10%) is continuously regenerated. The regeneration is achieved by the application of a sodium chloride solution (10%) for about 30 min. Continuous regeneration allows the efficiency of the treatment to be kept constant (as well as keeping constant the quality of the treated water) and avoids the need for stopping the plant for regeneration. As turbidity does not affect the efficiency of the treatment, the most important advantage of the MIEX® process is its applicability to the treatment of raw water. However, a solid–liquid separation is recommended as the downstream treatment for ensuring the removal of suspended solids and resin fines eventually carried over (Slunjski et al. 2000; Singer & Bilyk 2002). MIEX® resin is highly selective for low molecular weight DOC components and the main inorganic anion in competition with dissolved organic substances is SO\(_4\)^2- (Fu & Symons 1990; Fearing et al. 2004; Humbert et al. 2005). Bench-scale, pilot-scale and full-scale studies on MIEX® process applications have been presented in the literature. In these studies, good results were obtained in terms of DOC removal, coagulant dose reduction and disinfectant dose reduction in downstream treatments (Slunjski et al. 1999; Semmens et al. 2000; Cook et al. 2001; Delphos et al. 2001; Hamm & Bourke 2001; Drikas et al. 2003; Hammann et al. 2004; Boyer & Singer 2006). The experimental investigation presented in this paper was carried out at bench-scale at the DWTP of Florence (Italy) on raw water from the Arno River. Operational parameters, such as contact time and resin dose, were evaluated in preliminary experimental trials. The MIEX® resin treatment was simulated by a sequence of batch trials for the evaluation of both dissolved organics removal and the effects on downstream treatments. In particular, the effects on the coagulation process were evaluated in terms of coagulant dose reduction and the effects on the final disinfection process were evaluated in terms of disinfectant dose reduction.

**MATERIALS AND METHODS**

**Raw water**

Raw water from the Arno River from the “Anconella” DWTP (managed by Pubilacqua Spa) was used for the experimental trials. This DWTP treats about 2,200 L/s of...
water and produces about 90% of the drinking water needs of Florence and the surrounding areas. The treatment train consists of a pre-oxidation with ClO₂, clariflocculation with polyaluminum chloride (PACl), high rate sand filtration, ozonation, granular activated carbon (GAC) filtration and, finally, disinfection with ClO₂. Table 1 shows the mean values of some parameters of Arno River raw water during the experimental period (05/06/06–23/10/06).

**Experimental trials**

The first phase of the experiment was carried out in order to establish the operational parameters (contact time and resin dose) for the following experimental phases. Different quantities of resin (2.5, 5, 7.5 and 10 mL) were dosed in completely mixed reactors filled with 1 L of raw water. After a contact time of 5, 15, 30, 45 and 60 min, respectively, conductivity and UV absorbance at 254 nm (UV254) were measured. Samples were filtered through a 0.45 μm membrane before UV254 measurement. The UV254 is known to be representative of dissolved organic carbon content (Schäfer 2001). Operational parameters that allowed a 50% UV254 removal were selected. The second experimental phase was carried out in order to evaluate the performance of the MIEX® resins by using a sequential-type reactor: 7.5 mL of resin was added to 1 L of raw water for 10 min and, after a settling period of 5 min, treated water was separated and the same resin was applied to another 1 L of raw water. The same procedure was performed for a fixed number of times up to 1,500 Bed Volumes (BV) of treated water. The BV value is the total volume of treated water per volume of resin applied and it represents the resin service. At the end of each batch of the series a 500 mL sample of treated water was collected to form a “composite sample” for the subsequent experimental trials. UV254 absorbance, conductivity and turbidity of the sample were measured and the effects on the clariflocculation phase (with polyaluminium chloride, PACl 9.5% as Al₂O₃) were evaluated by jar tests. The turbidity and UV254 absorbance of each sample of clarified water were measured and each sample was hence used for subsequent chlorination trials (with NaClO). Chlorine dosages were selected on the basis of the UV254 absorbance of the clarified water and in order to obtain a residual chlorine concentration at 60 min (typical contact time for the disinfection treatment). Clarified water samples were filtered (0.45 μm), dosed with NaClO and the residual chlorine concentration was measured after 5, 10, 15, 30, 40, 50 and 60 min. The effects of MIEX® pre-treatment on the disinfection phase were evaluated employing the following two conditions: constant PACl dosage and different NaClO dosages; different PACl dosages and constant NaClO dosage.

**Analytical methods**

The UV absorbance at 254 nm was measured with a spectrophotometer UV/vis Jenway-6305 with a 10 cm
quartz cell. DOC concentration was determined by the conductimetric method with a Sievers 820. The specific UV<sub>254</sub> absorbance (SUVA) was calculated as the ratio between UV<sub>254</sub> absorbance (m<sup>2</sup>mg<sup>-1</sup>) and DOC concentration (mg/L). The chloride ion concentration was measured colorimetrically by a thiocyanate method and the sulfate ion concentration was determined by a turbidimetric method. The residual chlorine concentration was measured by the DPD (N,N-diethyl-p-phenylenediamine) method.

RESULTS AND DISCUSSION

Selection of resin dose and contact time

Operational parameters were selected by kinetic trials in the first phase of the experimentation. UV<sub>254</sub> removal was measured over time for different resin dosages applied. Experimental results were fitted with the following function model:

\[ y = K_0 e^{(-\frac{K_1}{t})} \]

where \( y \) is the percentage of UV<sub>254</sub> removal achieved at the contact time \( t \), and \( K_1 \) and \( K_0 \) are model parameters. According to this model, \( K_0 \) corresponds to the maximum level of UV<sub>254</sub> removal at high contact time (\( t \to \infty \)), whereas \( K_1 \) is related to the rate of the ion exchange reaction.

For each resin dose, \( K_1 \) and \( K_0 \) were estimated by a least-squares method. The results from the model are presented in Figure 4(a, b). For each resin dose (with the exception of 2.5 ml/L), the selected function fitted the experimental data very well, as indicated by the \( R^2 \) values in Figure 4(b).

As the resin dose increased, the rate of UV<sub>254</sub> removal increased. Moreover, for every resin dose applied the maximum UV<sub>254</sub> removal was about 60%. For 10 ml/L and 20 ml/L resin dose the maximum UV<sub>254</sub> removal was quickly achieved. For lower resin dosages, however, longer contact times were required in order to reach equilibrium. In the following experimental trials 7.5 ml/L resin dose and 10 min contact time were used, corresponding to the objective of about 50% UV<sub>254</sub> removal on the basis of the modelled behaviour.

The low UV<sub>254</sub> removal obtained in this experimental phase is probably due to the low SUVA value of raw water samples (about 2 m<sup>-1</sup>(mg/L)<sup>-1</sup>), according to results reported by Singer et al. (2007).

Resin efficiency for DOC removal

Figure 5 shows the UV<sub>254</sub> removal during the resin service time, i.e. BVs of treated water. UV<sub>254</sub> removal reached a maximum at the first BV value (40–70%), decreasing at 1,000 BVs and remaining constant for BVs higher than 1,000. For the maximum resin service considered in this experimental study (1,600 BVs), the resin was not exhausted with a residual removal efficiency between 30–60%, depending on the UV<sub>254</sub> absorbance of the raw water. These results agreed with the study carried out by Clifford (1990) who observed exhaustion BVs as high as 60,000 BVs.

![Figure 4](https://iwaponline.com/aqua/article-pdf/58/1/41/401347/41.pdf)
In order to confirm the UV\textsubscript{254} removal as indicator of the DOC removal, both parameters were measured on the same water samples. Table 2 shows the results of MIEX\textsuperscript{®} treatment efficiency in terms of DOC, UV\textsubscript{254} and SUVA.

As shown in Table 2, UV\textsubscript{254} removal was between 60 – 50%, DOC removal was about 30% and SUVA removal was between 40 – 30%.

The conductivity of treated water was measured in order to control the increase of the chloride ion concentration during the resin service (Figure 6). After the first contact with the resin, conductivity increased slightly from 1 to 9% followed by a return to the initial value. The slight increase of conductivity initially measured was ascribed both to the release of residual Cl\textsuperscript{2} from the virgin resin voids and, to a lesser extent, to the ion exchange between DOC\textsuperscript{2} and Cl\textsuperscript{2}. On the basis of these results conductivity was not considered a valid control parameter for the MIEX\textsuperscript{®} treatment efficiency.

Due to the fact that, in river water sources, SO\textsubscript{4}\textsuperscript{2} ions are typically found to be in competition with DOC\textsuperscript{2} in the exchange process, the sulphate ion concentration was measured during the resin service time. The chloride ion concentration was also measured in order to confirm the conductivity results. As shown in Figure 6, the chloride ion concentration reached a maximum at the first BV value and decreased to reach the initial value at 650 BVs, confirming the agreement between the chloride ion concentration and the conductivity.

As is typical of Type I SBA resin, MIEX\textsuperscript{®} is more selective for sulphate than chloride ions, primarily due to the double charge present on the sulphate ion. Consequently, chloride ions on the resin were rapidly exchanged for sulphate ions when initially put in contact with the water. This was shown by the increase of the chloride ion concentration and the simultaneous decrease in the sulfate ion concentration. Once this mechanism was exhausted, sulphate and chloride ion concentrations returned, at around 650 BVs, to the normal influent level. During subsequent operations the DOC\textsuperscript{2} replaced both residual chloride and the majority of the sulphate ions on the active sites of the resin.

**Effects on clariflocculation phase**

MIEX\textsuperscript{®} pre-treatment effects on clariflocculation phase were evaluated in terms of UV\textsubscript{254} removal and turbidity.

**Table 2** | UV\textsubscript{254} absorbance, DOC concentration and SUVA values during resin service time

<table>
<thead>
<tr>
<th>BV (–)</th>
<th>UV\textsubscript{254} (m\textsuperscript{-1})</th>
<th>DOC (mg/L)</th>
<th>SUVA (m\textsuperscript{-1} mg/L)</th>
<th>UV\textsubscript{254} removal (%)</th>
<th>DOC removal (%)</th>
<th>SUVA removal (%)</th>
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</thead>
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<tr>
<td>0</td>
<td>7.58</td>
<td>3.64</td>
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<td>1.36</td>
<td>55.54</td>
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<td>34.48</td>
</tr>
</tbody>
</table>
removal. In order to evaluate these effects, jar tests were carried out both on raw water and on MIEX® pre-treated water. A suitable range for the coagulant dose was selected depending on raw water quality (Table 3).

MIEX® pre-treatment alone outperformed clariflocculation in almost all cases and, when combined with coagulation, even at significantly reduced doses of coagulant, MIEX® pre-treatment always outperformed traditional clariflocculation (Figure 7). In MIEX® + clariflocculation the additional UV$_{254}$ removal during the subsequent clariflocculation phase depended on the quality of MIEX® pre-treated water: the higher the UV$_{254}$ removal during MIEX® treatment the lower the additional UV$_{254}$ removal after the subsequent clariflocculation process. Moreover the additional UV$_{254}$ removal seemed to be independent of coagulant dosage applied, whereas in conventional clariflocculation UV$_{254}$ removal increased as coagulant dosage increased (Figure 8).

Clarified water turbidity was measured for different coagulant dosages after MIEX® + clariflocculation and clariflocculation treatment. The turbidity decreased as the coagulant dosage increased to reach a minimum value independent of the coagulant dosage applied.

As presented in Figure 9, this behaviour was observed for both MIEX® + clariflocculation and clariflocculation treatments, but using MIEX® + clariflocculation the minimum turbidity value was reached with a lower coagulant dosage. These results are in accord with those obtained in previous studies (Delphos et al. 2001; Singer & Bilyk 2002).

On the basis of these results, a coagulant dosage was established in order to obtain a 2 NTU turbidity goal in the clarified water, depending on raw water turbidity, both for

| Table 3 | Quality of water used in the experimental trials (experimental period: 05/06/06–23/10/06) |
|---------|----------------------------------|----------------------|---------------------------|
| Water quality | Turbidity (NTU) | UV$_{254}$ | PACl dosage (ppm) |
| A        | <10                   | 0.500–0.700   | 5–25               |
| B        | 20–30                 | 0.800–0.900   | 5–80               |
| C        | 100–150               | 1–1.200       | 20–180             |
| D        | 700–800               | 1.500–2.000   | 50–250             |

Figure 7 | UV$_{254}$ removal obtained by using clariflocculation, MIEX® process and MIEX® + clariflocculation, depending on raw water turbidity and coagulant dosage applied.
MIXÉ pre-treated water and for conventionally treated water. As presented in Figure 10, the MIXÉ pre-treatment allowed a coagulant reduction between 40–60%, depending on raw water turbidity.

Moreover, during the experimental trials it was observed that flocs formed in the MIXÉ pre-treated water were bigger than those observed in traditional clariflocculation treatment. Larger floc sizes are likely to enhance settling and may therefore explain the lower turbidity levels observed at significantly reduced coagulant doses.

**Effects on chlorination phase**

The disinfection phase was simulated at bench-scale by adding NaClO to MIXÉ pre-treated–clarified–filtered water and to clarified–filtered water. During the disinfection, for a fixed coagulant dose, the residual chlorine concentration in MIXÉ pre-treated water was higher than in non-pre-treated water for the whole range of NaClO dosage applied (Figure 11).

Considering a typical disinfection contact time of 60 min, for each NaClO dose applied the residual chlorine concentration in MIXÉ pre-treated water was 15% higher than in non-pre-treated water (Figure 12). The effects of MIXÉ pre-treatment on the disinfection phase were also evaluated for different coagulant dosages applied in the previous clariflocculation process.

The residual chlorine concentration measured in MIXÉ pre-treated water was independent of the coagulant dosage.
dosage applied and always higher than in not-pre-treated water (Figure 13).

Moreover, in conventionally treated water residual chlorine concentration increased as coagulant dosage increased. Figure 14 shows the residual chlorine concentration after 60 min contact time both in resin pre-treated water and in non-pre-treated water for different coagulant dosages.

As expected, the residual chlorine concentration in MIEX® pre-treated water was higher than in non-pre-treated water and the difference in chlorine concentration between the two types of samples decreased as the coagulant dosage increased. For a given chlorine residual concentration, water pre-treated with resin consumed less chlorine than non-pre-treated water.

MIEX® pre-treatment reduces the DOC concentration and allows a reduction of the chlorine dosage in the subsequent disinfection phase. All these results are in accord with those reported in previous studies (Morran et al. 1997; Drikas et al. 2003). As chlorine consumption is expected to be directly related to disinfection by-products (DBPs) formation (Nikolaou et al. 1999; Collivignarelli & Sorlini 2004), MIEX® pre-treatment is likely to lead to a reduction of the DBPs concentration in the distribution network.

Figure 13 | Residual chlorine concentration during disinfection contact time for different coagulant (PACl) dosages applied and for a fixed disinfectant (NaClO) dosage of 3 mg/L as Cl2 (Raw water: water D.).
CONCLUSIONS

The experimental evaluation of MIEX® pre-treatment for drinking water production presented in this paper led to the following considerations:

- Resin pre-treatment achieved a UV254 removal between 40–70% depending on the UV254 absorbance of the raw water.
- The UV254 removal was 50–60%, the DOC removal was about 30% and the ratio between UV254 and DOC remained relatively constant in the operational conditions employed in this study. UV254 absorbance was confirmed to be a good indicator for the evaluation of the DOC concentration and for evaluating the MIEX® treatment efficiency.
- In conventional treatment processes the percentage UV254 removal during clariflocculation was proportional to the coagulant (PACl) dosage applied. To achieve the same efficiency as the MIEX® resins, conventional treatment required considerably higher coagulant doses.
- For a turbidity goal of 2 NTU in the clarified water, the required coagulant dosage with MIEX® pre-treatment was 40–60% lower than without pre-treatment, depending on the turbidity of the raw water. This reduction possibly reflects on clariflocculation sludge production.
- For each chlorine dosage applied, in MIEX® pre-treated water the residual chlorine concentration after 60 min contact time was 15% higher than in non-pre-treated water.
- In MIEX® pre-treated water the residual chlorine concentration was independent of the coagulant dosage applied in the previous clariflocculation phase and always higher than in non-pre-treated water. Without resin application the residual chlorine concentration increased as coagulant dosage increased.
- MIEX® pre-treatment reduces chlorine dosage required for the final disinfection and, therefore, is likely to lead to a reduction of the DBPs formation.
- On the other hand, the slower kinetics of decay of chlorine for MIEX® treated water could improve the distribution system management in maintaining chlorine residuals while applying less chlorine.

All the above-mentioned considerations show an important improvement as a result of the introduction of the MIEX® treatment, with an important reduction of the required coagulant dosage. Nevertheless, in order to evaluate the sustainability of a full-scale application of the process it would be necessary to compare the benefits with the costs (resins, facilities, reactants, energy, manpower, etc.). Further pilot-plant and full-scale experimental studies are, consequently, necessary to determine the possibility of a widespread diffusion of the MIEX® technology for river water treatment.

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