USE OF MAGNETIC ION EXCHANGE TO IMPROVE DOC-REMOVAL

by JARMO SALLANKO¹, VIRVE MERISALO¹, MARIN SLUNJSKI² 1 University of Oulu, P.O. BOX 4300, 90014 University of Oulu, Finland e-mail: jarmo.sallanko@oulu.fi, virve.merisalo@ymparisto.fi 2 Orica Watercare Europe, Roburite Centre, Shevington Wigan, Lancashire WN6 8HT United Kingdom e-mail: marin.slunjski@orica.com



Abstract

Problems associated with the amount of dissolved organic carbon (DOC) in drinking water treatment are very common. They range from the very obvious ones like treated water taste and odour and appearance, to the less understood disinfection by-product formation, bacterial regrowth in distribution network, exhaustion of activated carbon, membrane fouling and increased coagulation chemical demand. Ion exchange resins are known to be a very effective way of removing a reange of water contaminants, however high capital costs, scale-up issues and – resin fouling have limited the number of drinking water treatment applications. The magnetic ion exchange resins process (MIEX^{®1}) is one way to try solve these problems. In this paper the principle of MIEX[®]-process is introduced. Also results are presented of lab scale evaluations of MIEX[®]-process on two ground and one surface water from Finland. With all three waters the use of MIEX[®] pre-treatment resulted with a significantly improved final water quality as well as in a considerable decrease in the downstream coagulant requirements.

Key words - water treatment, ion exchange, MIEX, DOC, TOC.

Introduction

Dissolved organic carbon (DOC) affects water treatment processes and the final quality of drinking water in many ways. A high amount of DOC in raw water will directly impact on a high coagulant doses being required. It also has a negative effect on the performance and regeneration requirements of activated carbon systems. In membrane filtration systems, DOC directly impacts on the cleaning requirements. Finally, in terms of water quality, increased DOC residual in the treated water has many disadvantages too. They range from the formation of disinfection by-products (DBP) and increasing disinfectant chemical needs, to treated water colour and taste and odour. In the distribution network, the residual DOC acts as a food source for micro-organisms promoting the bacterial regrowth in distribution network.

The magnetic ion exchange resin (MIEX®) process offers a more economical and effective way of using ion exchange resins in drinking water treatment plants. It differs from traditional resin processes in that the resin is not applied in a filter bed form but is suspended in water. The resin is quite fine, with the mean particle diameter measuring only 180 μ m, which results with the fast kinetics of ion exchange. The resin's magnetic properties provide for a quick sedimentation of the resin agglomerates, making it possible to achieve resin recovery rates of over 99.9% at a gravity settler (clarifier) surface loading of 15 m/h.

MIEX®-process consist of rapid mixing, where resin is mixed with the raw water, and sedimentation, where the resin is recovered by settling and then pumped back to the rapid mixing/contactor stage (Figure 1). About 5–10 % of resin recycle is diverted to regeneration vessel, where the resin is regenerated with brine (NaCl).

MIEX® treatment is typically applied as the first unit operation in a multi-stage water treatment plant. It may also be applied as a post-treatment (ie. a polishing step), however in that case a filtration step is required to remove the small amount of resin carryoner from the settler.



Figure 1. MIEX® process flowchart.

The first full scale MIEX® plant was commissioned in 2001 at Wanneroo, Western Australia. The Wanneroo groundwater treatment plant utilises a number of water wells, and the quality of raw water varies quite a lot. Before installing MIEX® this plant suffered a number of problems associated with DOC. Nowadays the water treatment process includes MIEX® and chemical sedimentation which together achieve over 75 % DOC reduction. With MIEX®-pre-treatment the need for coagulation chemicals has reduced to one third of the previous levels. Furthermore, the need of chlorine has dropped from 6,9 mg/l down to 4,1 mg/l combined with a very large reduction in DBP formation (Orica 2004). In many other places the suitability of MIEX®-process is tested at lab and pilot scales (Cadee et. al. 2000, Bourke 2001, Härmä et. al 2004,)

Matherials and methods

The aim of this study was to determine suitability of MIEX®-process for the treatment of three Finish raw waters. Those treatment plants are situated in northern part of Finland. One of the plants was surface water plant in Oulu which uses the water from Oulu River. The two other are ground waters – water from Liminka and the Lappavesi water which is treated by a two-pronged chemical treatment for organic and iron removal were tested. Average quality of those raw waters is described in Table 1.

This was a two stage study. In the first stage the required MIEX® resin concentrations and contact times were defined. These tests where made on the lab scale using 1000 ml vessels. The resin concentrations tested ranged between 5–20 ml/l. Treated water samples were taken between 2–30 min of mixing. The measured parameter was UV₂₅₄-absorbance. The above tests were used to select the required resin concentration and contact time.

In the second stage all tested waters were contacted with 10 ml/l resin and 15 min contact time. The resin was reused a number of times with 5 min allowed for resin sedimentation in between each re-use. In this way the resin was contacted with water 20 times in sequence with no regeneration. The waters from the first 15 jar tests were combined in a composite sample to produce a larger water sample that was representative of the resin used in a continuously operated proces.

Next, coagulation jar tests were conducted. In all cases the coagulation jar test procedure comprised 1 minute of fast (flash) mixing, 10 minute slow mixing (flocculation time) and 1 hour of sedimentation time. The coagulation jar testing was done on:

 raw waters directly, without the MIEX[®] pre-treatment using the chemical doses and pHs normally applied in the respective water plants,

Table 1. Average quality of raw waters.

Parameter	River Oulu	Ground- water Liminka	Ground- water Lappavesi
pН	6.9	6.3	6.1
DOC mg/l	9.5	4.6	9.0
Alkalinity mmol/l	0.2	0.6	0.3
Fe mg/l	0.48	5.10	12
Mn mg/l	0.03	0.11	0.25
CO ₂ mg/l	3	36	35
O ₂ mg/l	11.4	2.1	_
Hardness mmol/l	0.13	0.2	0.4

- MIEX®-treated water (composite samples) using one third of the plants' coagulant doses with no pH-adjustment, and finally
- MIEX®-treated water using one third of the typical coagulant doses with pH adjustment to optimise the coagulation conditions.

Results

Oulu

Water Plant Oulu uses surface water from River Oulu. The coagulant used at this plant is PIX-322 (iron salt) and the process is dissolved air flotation. Typical coagulant dose is $43 \mu l/l$ ($66g/m^3$) and pH is 4.5-4.7.

The first resin jar test in the sequence conducted with at 10 ml/l resin concentration and 15 minutes contact time achieved 97 % UV-absorbance reduction. The 20 times sequential resin reuse produced a composite sample with overall 86 % UV-absorbance and 59 % DOC reduction, with the final DOC level of 3.1 mg/l.

Coagulation only jar test with 43 ul/l PIX 322 produced a slightly better DOC residual of 2,6 mg/l.

Combination of MIEX® and 14.5 ug/l PIX coagulation treatments produced the best results, with the DOC residual of only 1,8 mg/l regardless of whether pH adjustment was conducted or not (Figure 2).



Figure 2. Amount of DOC in the raw water of water plant Oulu and after different treatments.

Water Plant Liminka uses groundwater from 3 wells. The coagulant used at this plant is Ekoflock 91 and the process is chemical precipitation. Typical coagulant dose used is 50 µl/l and pH is 7.1.

It shall be noted that in Liminka the goal of chemical treatment is more iron precipitation than the DOC removal, hence pH adjustment for optimised organic removal actually produced an inferioe result (Figure 3).

With MIEX[®] treatment only, the amount of DOC is reduced to nearly half the original level. The combined MIEX[®] and reduced dose Ekofloc treatment achieved a DOC reduction of 50 %.

Lapua

Water Plant Porrasoja in Lapua has 3 different water fractions with different treatments: alkazing by lime, chemical precipitation by PAX for iron removal and filtration for Mn removal in pH 8¹/₂, chemical flocculation and flotation for humic substances and after flotation water combine to the flow going to chemical precipitation for Fe.

In this study the water used was the fraction which goes first to flotation for organic material removal. The flocculation chemical used in flotation is 50 ul/l PAX XL60 and the flocculation pH is 6.2.

The flotation fraction water from Porrasoja appeared to be very suitable to MIEX® treatment. During preliminary tests, already at the resin concentration of 5 ml/l and 2 minutes contact time a 95 % UV absorbance reduction was achieved. The 20 sequential resin use treatment on it's own achieved 58 % DOC reduction, while the coagulation only treatment at 50 ul/l PAX and pH 6.2 achieved only 47 %. The reduced coagulant dose



Figure 3. Amount of DOC in the raw water of water plant Liminka and after different treatments.



Figure 4. Amount of DOC in the raw water of water plant Porrasoja and after different treatments.

treatment of MIEX[®] pre-treated water failed to further increase the DOC removal regardless of the coagulation pH used (Figure 4). Based on that when a combined treatment of this water is considered for Lapua the MIEX[®] resin concentration required may be lower than 10 ml/l, perhaps 5 µl/l.

Discussion and conclusion

MIEX[®]-process was in these laboratory study proved to be an effective way for DOC removal from Northern Finalnd waters. Tests made on the one surface and two ground waters demonstrate that by including a MIEX[®] pre-treatment step it is possible to significantly reduce the coagulant requirements (60%-70%) less than the current plant operation) while still improving the overall DOC removal by 10\%.

In one of the waters studied MIEX®-treatment on it's own produced a very good result.

Another conclusion from this study is that coagulation pH does not need adjusting when MIEX®-pretreatment is used.

Note

¹ MIEX[®] is a registered trademark of Orica Australia Pty.Ltd.

References

- Bourke, M. 2001. Use of a continuous ion exchange process (MIEX®) to remove TOC and sulfides from Florida water supplies. Jacksonville, Florida, USA, Orica Watercare Inc [online], viitattu 15.06.2004, http://www.miexresin.com/ BUSINESS/CHE/watercare/CHE00140.NSF/Page/ Published_Papers_Published_in_USA_2001-2004>
- Cadee, K., Slunjski, M. & Tattersall, J. 2000. MIEX® resin water treatment process. Amsterdam, The Netherlands [online], viitattu 20.06.2004, <http://www.miexresin.com/ BUSINESS/CHE/watercare/ CHE00140.NSF/Page/ Published_Papers_Published_in_other_countries >
- Härmä, V. & Toivanen, E. 2004. Orgaanisen aineen poistokokeet MIEX-prosessilla (Tests of organic material removal by MIEX[®]-process in finnish with English abstract). Vesitalous 1. p. 30–35.
- Orica 2004. Full Scale Application of MIEX® DOC resin at Wanneroo ground water treatment plant. Australia, Orica Advanced Water Technologies [online], viitattu 15.06.2004, http://www.miexresin.com/BUSINESS/CHE/watercare/ rwpattach.nsf/PublicbySrc/Wanneroo.pdf/\$file/Wanneroo. pdf