MIEX® DOC PROCESS
for Removal of Humics in Water Treatment

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INTRODUCTION

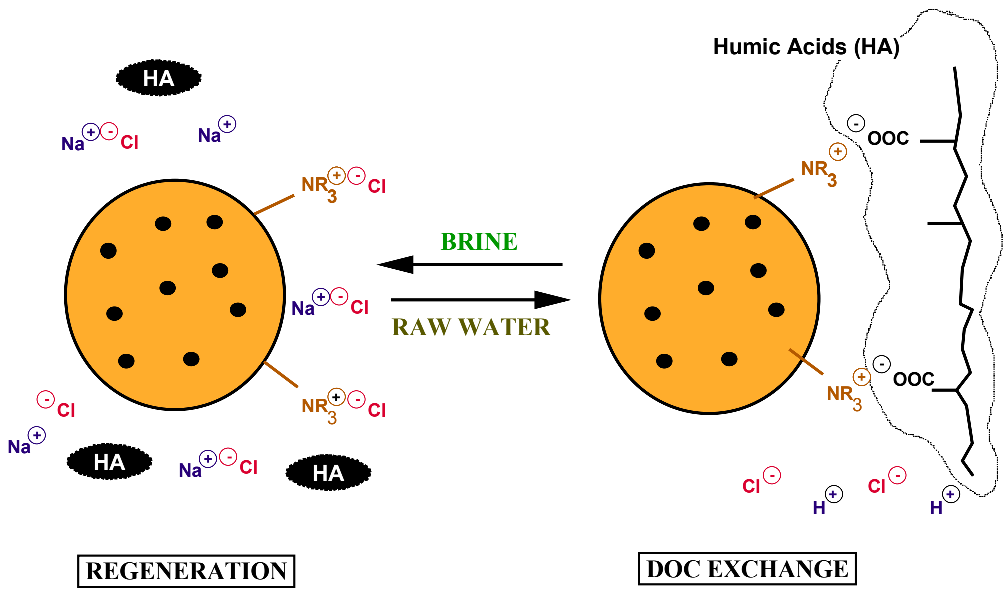
Humic substances present a significant problem in water treatment by causing colour in water, increasing required coagulant doses, providing precursors for disinfection by-products and causing re-growth in the distribution network.

Humic compounds comprise more than 60% of natural organic matter in source waters. Dissolved organic carbon (DOC) is a "bulk" measure of the organic matter content widely used in water treatment. Hence, in this paper the removal of humics is referred to as the DOC removal.

CHEMISTRY OF DOC EXCHANGE

DOC removal by ion exchange resins is based on the humic substances' weak organic acid character. The process is reversible which is its main advantage over other DOC sorption processes (fig 1).

Figure 1: **Chemistry of DOC Exchange**



The DOC sorption part of the exchange cycle is based on the high affinity of anionic resins for DOC. This allows DOC to be removed from raw waters containing low levels of DOC and other naturally occurring anions.

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The DOC de-sorption, ie. resin regeneration, is achieved by reversing the sorption reaction. For this, the resin is treated with a NaCl solution, usually 10%. Because of the high chloride concentration in liquid phase, the DOC is forced off the resin and replaced with chloride ions. Usually, NaOH (2%) is also added to brine to improve regeneration process efficiency by an increased DOC solubility at higher pH.

This general DOC exchange chemistry, utilised by conventional ion exchange processes, is also used in the MIEX® DOC Process[1].

MIEX® DOC RESIN

The MIEX® process is based on the new, patented, MIEX® DOC resin. This resin was specially developed to combine a number of ion exchange resin features generally believed to result in efficient removal of DOC and provide high organic fouling resistance (Slunjski et al, '99). It has a poly-acrylic, macroporous structure with a medium pore size and porosity. It also contains a high concentration of strong base, quaternary ammonia functional groups.

The MIEX® resin particle size is 2-5 times smaller than conventional resins, which are restricted to larger particles due to high fixed bed head losses. Smaller resins show higher rates of exchange because they have larger external specific surface area, hence more active sites on the surface of beads. As a result, the reliance on slow, particle diffusion controlled DOC exchange associated with active sites inside resin beads, is correspondingly reduced.

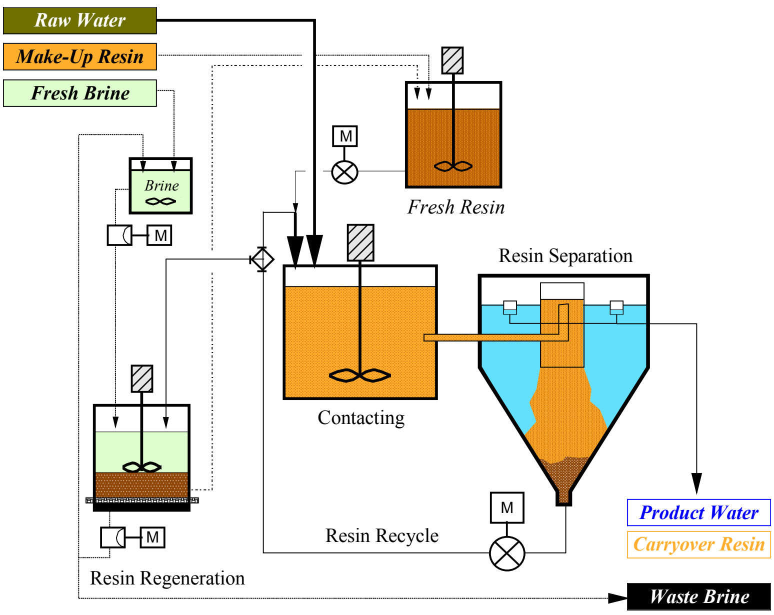
Another special feature of this resin is a high content of a magnetic compound, integrated into the resin structure. Because of this, the resin beads behave like small magnets, which is utilised in the resin recovery stage of the process.

MIEX DOC PROCESS

MIEX plants are very different from conventional ion exchange plants (fig 2).

Figure 2:

MIEX® DOC Process Flowsheet



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MIEX® Process - DOC Removal

The MIEX® reactor is a continuous, stirred tank reactor (CSTR). It has two inlet streams – raw water and resin (fig 2). The DOC exchange takes place while resin is suspended in water. The positive effects of uniform, high rate mass transfer in a mixed reactor, are combined with the high rate of MIEX® resin DOC exchange.

Detention time in the reactor is usually 30 minutes. This is 3-6 times longer than the empty bed contact time in conventional fixed bed systems. Resin concentration in the reactor is maintained at 0.5%-1.0% v/v, depending on the raw water DOC level.

Most of the inlet resin is made up of the recycled resin recovered from the resin separator. A small amount of the resin recovered from the separator is continuously removed for regeneration, and is replaced with the same amount of fresh (regenerated) resin (fig 2). This continuously maintains the reactor DOC exchange capacity at a constant level, resulting with a constant quality of product water.

MIEX® Process - Resin Recovery

Flow out of the reactor to the separator is by gravity. Resin flows together with water. The separator inlet section (fig 2) is designed very much like a flocculating feedwell, ie. with hydraulic conditions to maximise inter-particle collisions which result in the magnetic agglomeration of individual resin beads. These resin agglomerates are capable of gravity settling against a high up-flow of water (7-15 $m^3m^{-2}h^{-1}$) towards the separator overflow. The high up-flow rate results, not only in a compact design of the separator, but also continuous resin “backwash” conditions that ensure no turbidity build up in the resin.

Settled resin concentrates on the bottom of the separator and is pumped back to the reactor inlet. This unique way of resin handling is possible because of the resin’s exceptional flow characteristics and resistance to physical attrition, both resulting from its small size and special formulation of the resin matrix.

MIEX® Process – Resin Regeneration

As previously mentioned, a small amount of the resin recovered from the separator is continuously removed from the recycle stream and replaced with fresh (regenerated) resin. The removed resin is regenerated “off-line”, in batches.

When a sufficient amount of used resin is accumulated in the regeneration vessel, carrier water is removed and the resin is contacted with a brine regenerant. Because of the uniform resin loading, the regeneration can be conducted in a column or a mixed tank. After regeneration, brine is drained off, the resin is rinsed with water and transferred to the fresh resin tank.

This regeneration process requires no resin backwashing and only very small amount of resin rinsing. Hence, it is very efficient with respect to water consumption and generation of waste. The waste stream is a highly concentrated DOC (humics) solution (up to 20 g/L DOC) in 8-10% NaCl which may have some commercial application.

SYNERGIES WITH CONVENTIONAL TREATMENT PROCESSES

The MIEX® process contributes to suspended solids through a small amount of resin carry-over from the separator (less than 1.5 mg/L). Hence, some form of post-treatment for turbidity removal will always be required.

Because the turbidity is allowed to pass through the MIEX® process, it can be used for the treatment of raw water as well as for polishing of conventionally treated water (fig 3). This was investigated during the Wanneroo Feasibility Study with results indicating a high degree of synergy between the MIEX® DOC Process and conventional alum treatment (fig 4).

Figure 3: **Process Options – MIEX® Process, Alum Coagulation & Filtration**

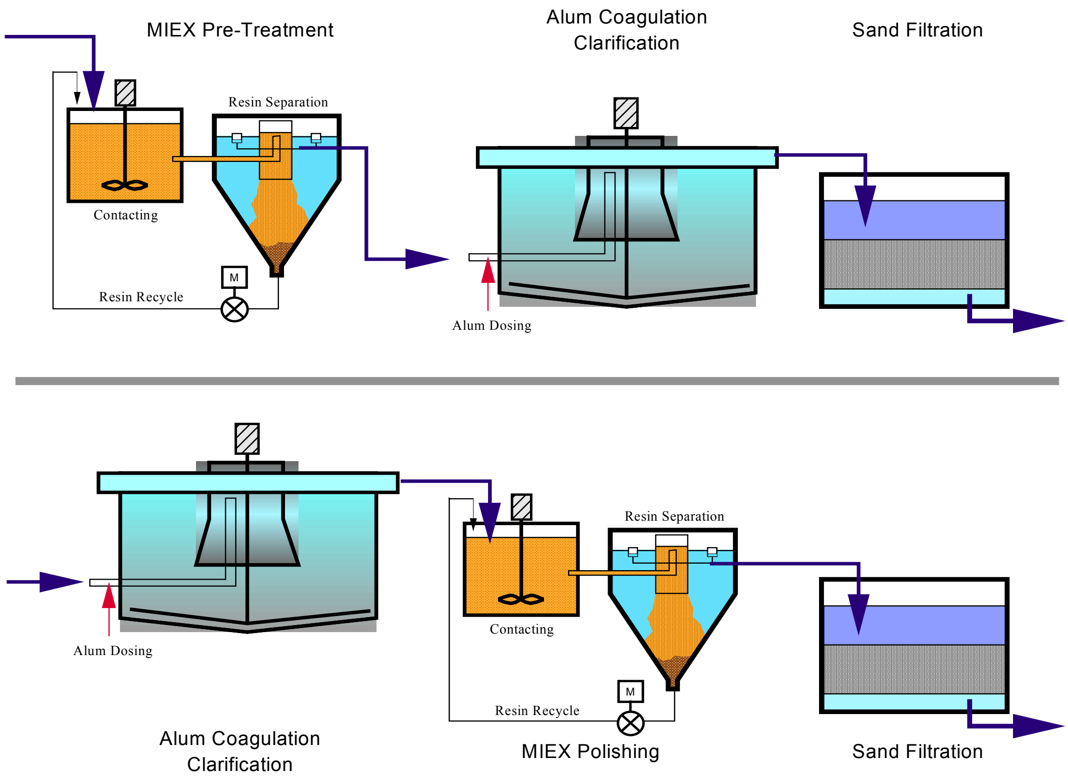
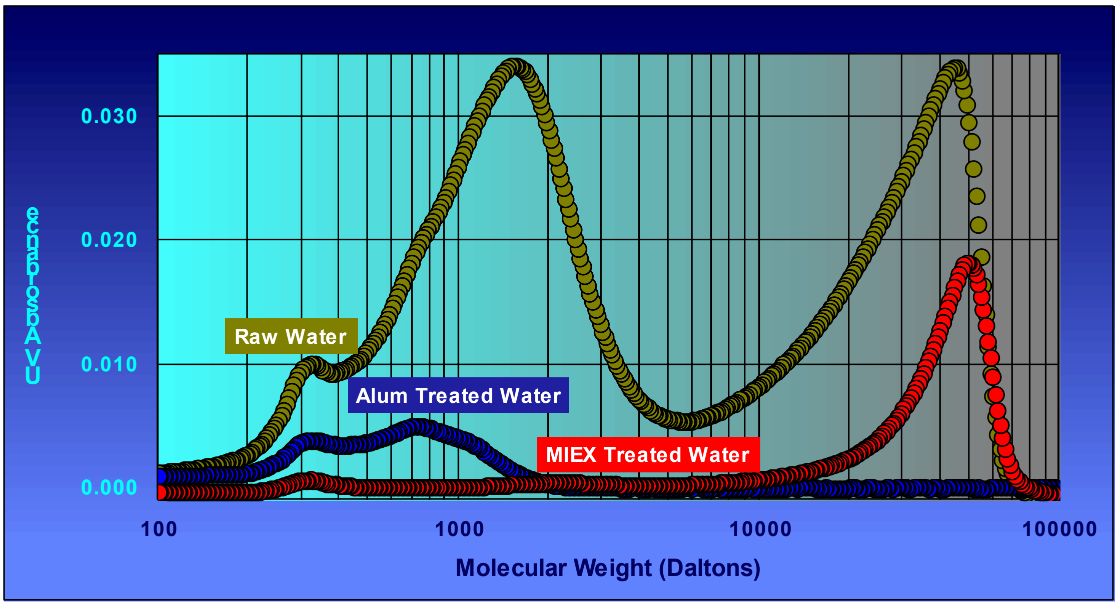


Figure 4: **SEC Profiles - Raw, (Enh) Coagulated and MIEX® Treated Water**

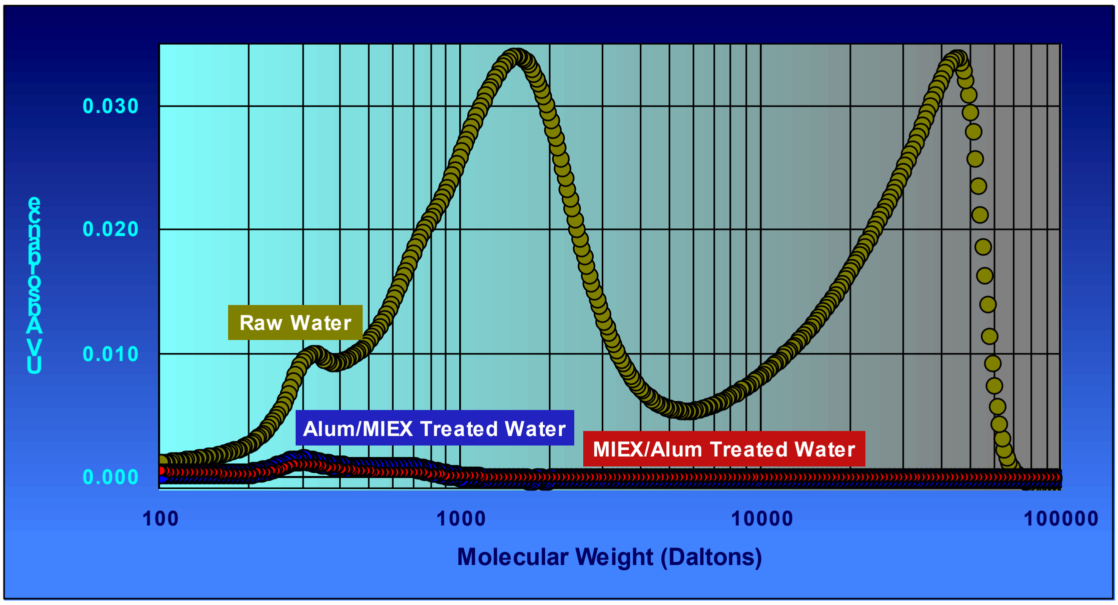


As the size exclusion chromatography (SEC) results show, the MIEX® process preferentially removed lower molecular weight substances from Wanneroo ground water. In contrast, alum treatment, even at high alum doses (90 mg/L alum) and modified pH (6.41), ie. "enhanced coagulation", left behind a significant amount of lower molecular weight DOC.

SEC profiles for combined treatments indicate almost complete removal of UV absorbing DOC (fig 5). These results are further confirmed by the corresponding DOC results:

- Enhanced alum coagulation treatment (90 mg/L alum, pH 6.41) followed by MIEX jar test (0.4% v/v resin, 30 min) reduced DOC from 9.5 mg/L to 1.5 mg/L, while
- MIEX jar test (0.8% v/v resin, 30 min) followed by alum jar test (30 mg/L) reduced DOC from 9.5 mg/L to 1.7 mg/L DOC.

Figure 5: **SEC Profiles for Combined Treatments**



SEC and DOC results indicate an almost identical treatment performance in both process sequences at Wanneroo. Hence, selection of the optimum sequence must be made based on the overall efficiency of each of the combinations with respect to chemical consumption and waste production. This work is still being progressed.

PROCESS DEVELOPMENT AND COMMERCIALISATION

The idea to use an ion exchange process for the removal of DOC in potable water treatment in Australia dates back to mid '80s (Bursill et al, '85). However it was in 1990, that a partnership was formed between Orica Watercare (then ICI), SA Water (then E&WS) and CSIRO Molecular Sciences with the aim of developing this idea into a commercially viable process.

This work started with the new resin produced and tested on the bench scale by CSIRO and SA Water - Australian Water Quality Centre (AWQC), respectively. Small pilot testing (7 LPM) followed this in '94 at AWQC (Morran et al, 1996). In '95, Orica and AWQC installed a 175 kLD pilot plant at Hope Valley (SA). This plant was used to further develop the design concept and test continuous process performance on the Hope Valley reservoir water (Nguyen et al, 1997).

In '97, the process was scaled up to 1 MLD and a pilot facility was installed at the WATER Corporation Wanneroo Ground Water Treatment Plant. This feasibility study, conducted jointly by Orica and WATER Corporation, investigated the effect of MIEX treatment on the removal of DOC and the removal of non-sulphide reduced sulphur (NSRS) compounds. NSRS is suspected to be the precursor for a "swampy" odour of water, occasionally formed in the Wanneroo water distribution system, which is the subject of customer complaints (Bourke et all, 1999). In addition, it was required to determine optimal operating parameters for the process, its long term efficiency in treating Wanneroo ground water, effect on the currently used conventional treatment process and estimate operating costs.

Now, after several years of an intensive development program, the MIEX® DOC Process is entering full commercialisation. In '98, in parallel with the application process development, Orica and CSIRO have embarked on the transfer of resin manufacturing technology to Orica. A medium size production facility was designed by Orica Engineering and is currently in the final construction stage. The first batches of the MIEX® resin from this facility are expected in mid 2000.

In August 1999, based on the feasibility study results that indicated the MIEX® process was very efficient in reducing DOC and NSRS levels in Wanneroo ground water, WATER Corporation announced their decision to construct a 225 MLD MIEX® DOC Process plant at Wanneroo. This project started in October '99 with the goal of delivering the world's first MIEX® facility in early 2001. The MIEX® plant will be integrated with the current treatment process with the additional operating cost partially offset by savings in alum and sludge production (Bourke and Slunjski, 1999).

In addition, already a lot of interest in the MIEX technology was shown in USA, where implementation of the new standards that regulate levels of Disinfection By-Products (DBP) makes it necessary for water utilities to search for new processes that can deliver enhanced DOC removal. At this time, pilot and bench scale trials are under way in Minnesota and North Carolina, with lot more activity expected in the near future.

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