Integrated Biological Filtration and Reverse Osmosis treatment of cold poor quality groundwater on the North American prairies

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Abstract Groundwater supplies on the Canadian prairies are often contaminated with arsenic, high levels of sulphate, ammonium or nitrate, iron and manganese as well as organic material. These typically brackish water sources (TDS levels >1000 mg/L) are supplying potable and nonpotable water requirements of water-short communities. The high cost of supplying better quality water (pipelines) to remote native communities sparked the development of water treatment processes that can effectively deal with local water sources. During the past four years treatment processes for these poor quality groundwater sources have been developed. A community with a long-standing boil water advisory (total duration 9 years), Yellow Quill First Nation, was selected for the initial evaluation and development of different water treatment processes. During a 20 month on-site pilot conventional (including manganese greensand), advanced (including ozone), and emerging (including biological) water treatment processes were evaluated. The most promising processes were biological and the majority of our effort was expended developing a combination of biological processes that could remove iron, bioavailable organic carbon and other microbial nutrients/energy sources including phosphorus and arsenic, and also oxidize 4 mg ammonium-N/L. This well water, when allowed to oxidize chemically, produced 0.5 million particles/mL, but biological oxidation (with the bacteria gaining energy from the oxidation process) prevented this particle formation and particle levels after biological filtration were less than 100 particles/mL. The objectives of the biological treatment were therefore to remove microbial nutrients and energy sources as well as preventing the formation of particles. Because of high salt levels and refractory dissolved organic material, the biologically treated water needed to be polished with reverse osmosis (RO) membranes. Particles can directly foul RO membranes and bacterial energy or nutrient sources promote the growth of bacteria with high risk of membrane biofouling. An integrated biological treatment process was developed to deal with all of these issues. Three biofilters operated in series provided different conditions suitable for the sequential purification of this extremely poor quality water source. Air was introduced ahead of the three filter units. This was to increase the redox potential to a range where bacteria can start the biological oxidation of iron. The full-scale water treatment process is a copy of one of the pilot systems and continued development in the full-scale plant has further increased its efficiency. Despite 6°C water, all of the ammonium is oxidized to nitrate, most of the arsenic and phosphorus is removed, and other bioavailable material (e.g., bioavailable DOC) is removed. After the biological filtration the water is biologically stable resulting in low biological fouling of the RO membranes with up to 18 months between membrane cleanings. The Yellow Quill Water Treatment Plant has been providing high quality drinking water to its 1,000 people for more than 2 years and the developed process has now been successfully piloted in three other water treatment plants. Two of these plants, Gordon and Pasqua First Nations, have now replaced their manganese greensand

filtration material with biological support material. The developed process offers the following advantages compared with the most commonly used conventional groundwater treatment process, manganese greensand pre-treatment ahead of RO membranes: 1)The biological filtration uses no chemicals, 2) The process is robust with few operator interventions, 3) It is highly cost-effective due to overall low chemical use, low antiscalant ahead of membranes and low chlorine doses required, 4) Inexpensive and long-lasting filtration material (Filtralite® Expanded Clay), 5) Continuous operation (can be > 30 days), 6) Long time interval between membrane cleanings (>1 year), 6) Increased longevity of RO membranes, 7) Time interval between filter backwashes >10 times greater and <5% backwash water is required, 8) Improved work quality for operators as backwashing and chemical handling is much reduced.

Keywords Aboriginal communities, ammonium, arsenic, bioavailable dissolved organic carbon, biological filtration, ground water treatment, iron, nitrification, Reverse Osmosis

INTRODUCTION

The regulation of drinking water quality has received increasing attention during the past decade with major waterborne disease outbreaks in North America and elsewhere. However, production of high quality drinking water at the treatment plant meeting all health and aesthetic guidelines may still not provide acceptable quality water at the kitchen tap. The reason for this is deterioration of quality in the distribution system (Geldreich, 1996). There are no guidelines anywhere that deal effectively with the cause of this problem, the presence of microbial nutrients in the treated water. Any compound capable of encouraging microbial growth is a concern including phosphorus, nitrogen, dissolved organic material, iron, manganese, and arsenic.

While some microbial nutrients, such as iron has an aesthetic guideline associated with it, even when this guideline is met low iron levels can provide an essential nutrient requirement for microbes growing in the distribution system. Others, such as nitrate and arsenic, have health guidelines, but again the microbes can make use of these compounds at levels that are even lower than these guidelines. Several, however, such as ammonium, phosphorus and dissolved organic material have no direct guidelines associated with them. Yet, these compounds are key requirements for the microbial communities that establish themselves as biofilms in drinking water distribution systems (Geldreich, 1996).

With no effective guidelines or regulations to curb the release of microbial nutrients in the distribution system it can be anticipated that even with better processes to treat the water, the quality of the delivered water can still be a concern. Indeed, virtually no presently used treatment processes are capable of effectively removing all microbial nutrients. It was long assumed that tight membrane technologies, such as nanofiltration and reverse osmosis, were capable of eliminating microbial nutrients in an effective fashion. It has, however, now been clearly shown that nanofiltration membranes provide a poor barrier for bioavailable organic material with proliferation of microbes in the treated water (Liikanen et al. 2003). Even a tight Reverse Osmosis (RO) membrane was only able to remove 42% of the compounds causing Biological Oxygen Demand (Al-Wazzan et al. 2002). This is especially interesting as the RO membrane rejected much smaller ions, such as sodium, by 99%.

Indeed, some conventional and advanced treatment technologies, such as ozonation generate microbial nutrients. Even chlorination before distribution can cause oxidation of DOC making it more bio-available (Prevost et al. 2005). Therefore most conventional and advanced

technologies are not able to produce finished water that is devoid of microbial nutrients with oxidative disinfection practices exacerbating the problems. The ensuing microbial growth can cause loss of chlorine residuals, development of taste and odour, and it can facilitate the proliferation of disease-causing microorganisms, such as *Legionella*, and *Mycobacterium* as well as repair and re-growth of coliforms etc., in the distribution system (Geldreich, 1996).

A major limiting factor when membrane technologies are implemented is microbial fouling of the membranes, which will decrease the quality of produced water and cause increased requirements for membrane cleanings and premature failure of the membranes (Baker and Dudley 1998). As tight membranes (Reverse Osmosis and nanofiltration membranes) are important parts of most advanced water treatment processes it is essential to remove compounds that can support microbial growth ahead of the membranes. Clearly, no conventional or advanced technologies can effectively deal with this. Emerging water treatment processes that incorporate microbial growth can, however, remove most of these compounds. It comes down to either grow the microbes in a controlled way in the water treatment plant or suffer the consequences of uncontrolled growth in membrane processes and distribution systems.

We have worked on including microbial water treatment processes for poor quality groundwater sources in aboriginal communities in Central Canada. A concern in implementing such treatments is the low temperature of the raw waters, which range from $5^{\circ}C - 10^{\circ}C$. With well depths from 100-200 m the water temperature is stable with no more than $1^{\circ}C$ seasonal variation for an individual well. Theoretically these low temperatures should result in much decreased microbial activities compared with higher temperatures impeding the development of biological water treatment systems. However, we have during the past 4 years developed treatment processes that are not only effective in removing microbial nutrients, they are also completed without chemical additions. These processes have also been integrated with reverse osmosis (RO) membrane treatment. A 20 month pilot and development study resulted in the design of an Integrated Biological and RO Membrane Treatment Plant, which was completed in December 2003 at Yellow Quill. On-site research has enabled optimization of the processes and two more plants, Pasqua and Gordon First Nations, were commissioned at the end of 2005.

METHODS

For the pilot study two refrigerated truck trailers (2.4 by 14.4 m) were outfitted with a laboratory, pilot-scale treatment units, office, living and eating quarters. These fully insulated trailers can withstand winter conditions down to -40°C and they were parked next to Yellow Quill's well heads. An insulated connection to one well was made and from July 2002, to March 2004 well water was continuously pumped at 200 L/min into the pilot trailer. This water was distributed by a header pipe on the wall close to the ceiling allowing simultaneous piloting of different processes. Pressure and gravity filters, chemical injectors systems, ozone and UV units were all easily connected in series to find which combination of treatments were most suitable. We had most success with a biological treatment combination consisting of one contactor followed by three filters (containing different types of aggregates for microbial adhesion) and the discussion in this paper centers around the trials with these units, which were followed by RO membranes. Due to the aggressive nature of this water we used plastic material wherever possible.

Samples for routine parameters, such as pH, redox potential, temperature, dissolved oxygen, iron, manganese, turbidity, colour, ammonium, and nitrate were carried out within minutes after

samples had been collected in the pilot system using mainly Hach equipment and methodologies. Our Hach equipment included oxygen, turbidity, redox and pH meters as well as several spectrophotometers (Hach DR 890, DR 2000, DR 3000, and DR 4000). For extensive metal analyses, ion coupled plasma-atomic emission spectrometry (ICP-AES) was used by an outside analytical laboratory. Dissolved organic carbon was analyzed using persulfate oxidation with a phenolphthalein colour reagent. Sulphate analysis was carried out using a turbidometric/spectophotometric analysis with barium sulphate. Analyses were carried out according to Standard Operating Procedures almost all adhering to the APHA.

RESULTS AND DISCUSSION

Background

This work originated at Yellow Quill First Nations, a native community of around 1000 people in Central Canada. Yellow Quill has had the longest boil-water-advisory in Canada for this size of community. The boil-water advisory was put in place in 1995 and it could not be lifted with the existing surface water source and water treatment equipment. A search for better quality source waters was not successful as good quality water that could possibly be used was one hundred kilometers away. Because communities like Yellow Quill are frequently remote with low populations, pipeline costs are high and while extensively used, heavy government subsidies have been the rule rather than the exception for such developments. But, as many of these water sources contain ample microbial nutrients, which are sometimes increased rather than decreased by conventional water treatment processes, the growth of disease-causing microbes and loss of chlorine residuals in long pipelines makes remote treatment and distribution less attractive.

The potential for local groundwater sources to supply these rural communities is positive in terms of quantity, but quality is frequently extremely poor. Despite concerns at Yellow Quill with high levels of iron, manganese, arsenic, dissolved organic carbon, ammonium, hardness and high TDS levels, it was decided that a pilot-facility be established to determine which treatment processes could possibly render this water drinkable. Conventional technologies, such as manganese greensand, were ineffective and while some other technologies were promising, such as ozonation, the floc generated resulted in short filter runs. While biological filtration was attractive, the temperature of the well water was only 6°C and its usefulness was not known.

Yellow Quill's ground water and other similar sources rapidly generate both scaling and fouling problems, which must be taken into consideration when designing the full-scale treatment systems. This also translates into problems with analytical equipment, such as various probes requiring frequent cleanings. Daily calibration of the redox probes was essential, and other probes were also frequently calibrated. Indeed, more than 20 redox probes were poisoned during the Yellow Quill pilot study. Even industrial in-line probes, such as Endress and Hauser redox probes, rapidly failed when exposed to marginally treated Yellow Quill groundwater. Before on-line probes are used it is essential to moderate the fouling properties of the water.

Yellow Quill's ground water source

Yellow Quill's wells are around 100 m into the ground resulting in rather cold temperatures year-round, around 5.5°C. Deeper wells have typically water temperatures 8-10°C. The water is high in TDS, and specific ions including iron, manganese, arsenic, ammonium, sulphate, as well as

hardness and dissolved organics. The chemical composition of the Yellow Quill raw water is shown in Table 1.1 with the Canadian Water Quality Guideline for the different compounds. This was the original water analysis from which we were basing our treatment needs. The ammonium-N level was above 10 mg/L, but after the wells were operational this decreased to around 4.0 mg/L. In contrast, manganese levels stabilized at higher rather than lower levels after the wells were drawn upon. The compounds that are above the Canadian Water Quality Guidelines in the table have been highlighted (DOC has also been highlighted as this level is too high to safely chlorinate without generating other problems).

Table 1.1 The composition of the Yellow Quill Raw water in the spring of 2001 in comparison to the Canadian Water Quality Guidelines (Health Canada, 1996).

| Constituent | Unit | Reserve Aquifer | GCDWQ | | |
|----------------------|------|-----------------|------------------|--|--|
| Inorganic Parameters | | | | | |
| Alkalinity | mg/L | 427 | 500 | | |
| Aluminum | mg/L | <0.005 | 0.1 | | |
| Arsenic | mg/L | 0.011 | 0.025 | | |
| Barium | mg/L | 0.008 | 1 | | |
| Boron | mg/L | 0.74 | 5 | | |
| Cadmium | mg/L | <0.001 | 0.005 | | |
| Chromium | mg/L | <0.001 | 0.05 | | |
| Copper | mg/L | <0.001 | 1 | | |
| Hardness | mg/L | 972 | 800 | | |
| Iron | mg/L | 7.6 | 0.3 | | |
| Lead | mg/L | <0.002 | 0.01 | | |
| Magnesium | mg/L | 92 | 200 | | |
| Manganese | mg/L | 0.21 | 0.05 | | |
| Nitrate | mg/L | <0.01 | 45 | | |
| pН | | 7.68 | 6.5-8.5 | | |
| Sodium | mg/L | 238 | 00 | | |
| Sulfate | mg/L | 1010 | 500 | | |
| TDS | mg/L | 2098 | 500 | | |
| Zinc | mg/L | <0.005 | 5 | | |
| Organic Parameters | | | | | |
| DOC | mg/L | 10 | Not in guideline | | |

Biological water treatment

In biological treatment of water microbes attached to filter media carry out the desired removal. The goal with biological removal of different compounds is to move these compounds into a particulate state either as a part of the microbial biomass or as organic/inorganic flocs that can be easily separated out. We have worked with GAC as well as expanded clay material (Filtralite[®]).

The processes used here is aerated biological treatment where oxidizing processes (bio-oxidation) are used and the microbes gain energy when they transform the ions from a reduced to an oxidized state (i.e., from Fe^{2+} to Fe^{3+} , Mn^{2+} to Mn^{3+} , As^{3+} to As^{5+} , and NH_4^+ to NO_3^- , Mouchet 1992). Biological treatment as discussed here is centred on establishing microbes that

will need to obtain energy (bio-oxidation) from the conversion and sequestration of compounds that we would like to remove from the water.

Therefore a key factor in biological treatment is the provision of oxygen which was introduced ahead of the first filter in a series of three biological filters (both air and oxygen was used). The majority of the oxygen consumed occurred in the last filter, which is the nitrification unit. Oxygen consumption rates >10 mg/L in 30 min are similar to oxygen consumption rates over a 3.5 month period in ice-covered lakes in Central Canada making the biological activity in Filter 3 some 5000 times greater than a highly biologically active natural aquatic system in a cold climate.

Biological iron removal

The key factors to be controlled during biological iron removal include establishing the correct redox potential and oxygen concentrations. To remove iron a redox potential of around 0 mV is desired, but the groundwater at Yellow Quill is around -100 mV. In addition, the water smells metallic and it was considered essential to remove the gasses giving rise to this smell.

Various means of changing the redox potential and removing the gasses were tested and the issue became how to introduce oxygen and what contact time was required. Several contactors were designed before one that allowed for an optimum increase of the redox potential was found. In the full-scale treatment plant several modifications to the contactor have been made. Iron removal rates can be variable and three determinations over a two-week period have been averaged in Table 1.2. All iron is removed by the biological process and even when challenged the residual iron levels after filter 3 are less than 0.05 mg Fe/L or >99.4% removal. Increasing redox potentials indicate complete iron removal and oxidation of ammonium (Table 1.2).

Table 1.2 The iron content, iron removal, % removal, and redox potential in the raw water and after the different treatment units (average of determinations for three different dates with standard deviation within brackets, water temperature 6°C)

| Filter Unit | Iron level (mg/L) | Iron removed (mg/L) | % Removed | Redox |
|-------------|-------------------|---------------------|-----------|----------|
| Raw Water | 8.15 | 0 | 0 | -82 |
| One | 2.30 (0.52) | 5.85 | 72 | -13 (12) |
| Two | 0.20 (0.09) | 2.10 | 26 | 60 (12) |
| Three | 0.01 (0.01) | 0.19 | 2 | 239 (8) |

Biological removal of arsenic, ammonium, and bioavailable organic carbon

The As compound of most concern is inorganic As^{3+} , which is more difficult to remove from solution using physical and chemical removal techniques than oxidized As^{5+} . Conventional processes use oxidizing compounds, such as chlorine, ozone and potassium permanganate to obtain this transformation. Microorganisms can, however, also carry out the transformation from As^{3+} to As^{5+} gaining energy in the process. While As^{3+} is poorly removed by RO membranes As^{5+} is effectively removed (Ning 2002). The biological process will convert As^{3+} to As^{5+} and when followed by RO membranes any remaining As will be removed. Arsenic can also coprecipitate with iron. The arsenic level in the Yellow Quill raw water was 10-12 μ g/L and removal to levels close to our detection limit of 2μ g/L was achieved by the biological filters.

Phosphorus is a compound that is similar to arsenic and arsenic's anion, arsenate, can be mistaken by microbes for the phosphorus' anion, phosphate, which is an essential nutrient. The phosphate level is close to our limit of detection at Yellow Quill even in the raw water.

Ammonium ions play a key part in water treatment because they need to be removed before breakpoint chlorination can be achieved. Oxidizing reagents, such as ozone, ClO₂, chloramines, and potassium permanganate cannot remove ammonium ions while chlorine reacts with the ammonium ions forming chloramines that are 10-100 times less potent than chlorine in terms of disinfection capacity (Degremont 1991). However, for every mg ammonium removed, the chlorine demand is around 10-15 mg making it a totally unsuitable process for Yellow Quill. Biological removal can be achieved by oxidation of ammonium to nitrate (nitrification). We were unable to generate a nitrifying population using the existing well water at Yellow Quill. Instead, we started searching for suitable nitrifying populations from uncontaminated natural water sources. This was successful and ammonium oxidation rates around 80% were achieved in the pilot units. During full-scale operation nitrification was discouraged (and no additions of any microbes were carried out), but after 8 months of operation nitrifying activity was evident. Modifications to the full-scale plant set out to encourage nitrification has now resulted in >98% removal of ammonium. Yellow Quill's ground water is "old" and only a small part of the DOC is bioavailable. Around ten percent of the DOC and 20% of the colour and UV-254 absorbing compounds were removed by the biological filters.

The biologically treated water was further polished in various Reverse Osmosis membrane combinations ranging from single stage to three stage units. Low fouling resulted in few opportunities to clean membranes and our practical knowledge in this area is still poor.

The Integrated Biological and RO Treatment Process

From the different pilot trials the groundwater treatment process that we developed for Yellow Quill First Nations include three biological filters run in series followed by an RO membrane treatment unit.

A summary of the chemistry of the groundwater coming in, the biologically treated water, and the membrane treated water is shown for some of the compounds that we were testing (many of them on a daily basis) in Table 1.3.

In terms of removals the biological filtration removed all iron, arsenic and most particles from the water. In addition ammonium was converted to nitrate and bioavailable DOC was also removed (although it is a small part of total DOC). Because of these biological removals we were able to run the membranes with extremely low fouling. The membranes could then effectively remove TDS, alkalinity, sulphate, DOC, colour and manganese. Under the conditions we were using we did not want manganese removal by the biological filtration units, but instead we used the membranes to remove the manganese. We have worked with several scenarios where ammonium removal rates have been optimized or indeed minimized as this ion can also be removed by some membranes.

A water treatment plant was constructed incorporating the developed biological and RO membrane processes. After 9 years of continuous boil water advisories Health Canada was able to lift the boil water advisory in March 2004 and the community has enjoyed high quality drinking water since that time. The plant has operated well with few challenges and two more plants were commissioned in the winter of 2005.

Table 1.3 The chemistry of the raw water, biotreated water and membrane treated water. Compounds affected strongly by biological filtration are shown in grey, while compounds that are affected strongly by membrane filtration are shown in white.

| Chemical | Raw | BioTreated | Membrane Treated |
|-------------------|--------|------------|------------------|
| Iron (mg/L) | 8.15 | 0.01 | 0.00 |
| Arsenic (µg/L) | 12 | <2 | <2 |
| Ammonium-N (mg/L) | 4.25 | 0.87 | 0.03 |
| Nitrate-N (mg/L) | 0.02 | 2.94 | 1.08 |
| Particles (#/mL) | 428484 | 62 | 0 |
| Turbidity (NTU) | 99.6 | 0.2 | 0.1 |
| | | | |
| TDS (mg/L) | 1853 | 1766 | 123 |
| Alkalinity (mg/L) | 424 | 384 | 20 |
| Sulphate (mg/L) | 1022 | 1015 | 1.6 |
| DOC (mg/L) | 9.9 | 8.9 | 0.5 |
| Colour (TCU) | 10.7 | 8.5 | 2.4 |
| UV-254 | 0.093 | 0.075 | 0.002 |
| Manganese (mg/L) | 0.350 | 0.354 | 0.019 |

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