Treatment of 1,4-Dioxane in Groundwater using Advanced Oxidation Processes: UV/Peroxide, Ozone/Peroxide, and UV/Titanium Dioxide

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Abstract

In 2004, 1,4–dioxane was detected in the water supply of a groundwater treatment plant in Ontario, Canada. With no provincial regulations for 1,4-dioxane in place, the groundwater plant was proactively shut down. A treatability study was initiated to assess the suitability of various advanced oxidation process (AOP) technologies for effective reduction of 1,4-dioxane from the water supply. The study consisted of a literature review, bench-scale and pilot testing. Three AOP technologies were tested in this study. These included UV/peroxide, ozone/peroxide, and UV/titanium dioxide, all of which were capable of destructing 1,4-dioxane to low or non-detectable levels.

Key Words

Ultraviolet; UV; ozone; titanium dioxide; hydrogen peroxide; advanced oxidation; 1,4-dioxane.

Introduction

1,4-Dioxane (CAS # 123-91-1) is an emerging environmental contaminant of concern in potable water applications. 1,4-Dioxane readily seeps into groundwater, is not readily adsorbed onto soil particles, and is not easily biodegradable (Walsom and

Tunnicliffe, 2002). It can be somewhat difficult to treat due to its high solubility in water. 1,4-Dioxane is used as a solvent in polystyrene and latex production as well as in wood stains and varnishes.

The United States Environmental Protection Agency (USEPA) considers 1,4-dioxane a high production volume (HPV) chemical, which means its annual production and/or importation volume exceeds 1 million pounds (USEPA, 2006). Although not strictly regulated in North America, various states and provinces have set recommended target levels for this contaminant, between 2 and 85 ppb. Michigan's is the most stringent at a level of 2 ppb. The World Health Organization (WHO) considers 50 μg/L to be an appropriate guideline value for 1,4-dioxane in drinking water (WHO, 2005). In Ontario, the Ministry of the Environment is currently reviewing and is in the process of setting regulations for 1,4-dioxane in drinking water.

All advanced oxidation processes have a common thread – the generation of a highly reactive species, the hydroxyl radical (OH•). The various processes vary in which chemical is used to generate the hydroxyl radical such as hydrogen peroxide (H_2O_2), or titanium dioxide (TiO_2) and the means to initiate the reaction (UV, heat, etc.).

The rate of oxidation or degradation of a target pollutant is dependent on two main factors: the concentration of radicals and the concentration of the target pollutant (Parsons and Williams, 2004). Maintaining a sufficient radical concentration in the water matrix depends, to a large extent, on the concentration of radical scavengers (Parsons and Williams, 2004).

Radical scavengers such as alkalinity, chloride, and organics reduce the overall efficiency of the advanced oxidation processes by consuming the hydroxyl radicals before the radicals have a chance to react with the pollutants of interest. From the preliminary raw water quality testing conducted as part of this study, it appears that the groundwater poses some potential challenges for the AOP processes due to the high levels of several scavengers. In particular, the alkalinity of the wells is in the 200 to 300 mg/L as $CaCO_3$ range, which is relatively high for advanced oxidation. The chloride concentration ranges from 150 to over 200 mg/L in most of the wells. Chloride is theoretically a very efficient scavenger, however its impact is difficult to predict because there is reportedly a reverse reaction involving the chloride, which may re-form the radicals to a degree that depends on a variety of water characteristics. The scavenging ability of chloride may therefore be site-specific and difficult to predict without testing. Natural organic matter is also a radical scavenger whose effect on advanced oxidation depends on the character of the specific organics present. There is therefore a need to test the water at bench- or pilot-scale before being able to make predictions of AOP effectiveness.

Another important parameter to consider is bromide concentration, especially when considering employing an ozone treatment process, such as an ozone AOP. Ozone (O_3) reacts with bromide to form bromate, which has a 10 μg/L limit in drinking water in Ontario. As a general rule of thumb, bromide concentrations greater than approximately 50 μg/L indicate a high potential to exceed the bromate limit when ozonating at doses and contact times consistent with disinfection. Ozonation requirements for advanced oxidation are often greater than for disinfection, so the concern about bromate increases if an ozone AOP technology is used. However, at least one ozone-based AOP vendor has developed an ozone/hydrogen peroxide (O_3/H_2O_2) technology that uses carefully-controlled application of ozone and H_2O_2 to keep the ratio of ozone to H_2O_2 very low, which provides hydroxyl radical generation while minimizing bromate formation. This procedure is sound from a theoretical standpoint, but control over the ozone dosing is critical to avoid excessive bromate formation.

Based on industry experience, it was recommended that three AOP technologies be considered for subsequent bench-scale testing. These criteria included but were not limited to: full-scale technology experience, potable water treatment capability and experience, previously documented AOP treatment performance treating 1,4-dioxane and other contaminants, regulatory approval of AOP technology, and ancillary systems – chemical, power, residuals. These three most practical and promising AOP technologies that were selected for further study included UV/H_2O_2, UV/TiO_2, and O_3/H_2O_2.

Experimental

Bench-Scale Tests

In parallel to the bench-scale testing completed at the three equipment manufacturers' facilities, additional water quality testing was conducted at the University of Toronto (U of T) for representative quality assurance / quality control testing and for later comparison back to the equipment manufacturers' results.

The parameters tested in this study included scavenging potential, general water characteristics, and by-product formation including ethylene diformate, bromate, DBPs, and BDOC.

The hydroxyl radical (•OH) scavenging rate constant due to natural scavengers (ks) in the water was measured using a low pressure UV collimated beam apparatus. A probe material, in this case benzoic acid, was added to the water to set up a competition kinetics experiment. Several samples were prepared with varying doses of probe material (ranging from 0.2 to 5 mM). Each sample was dosed with excess H_2O_2 (50 mg/L) and irradiated under a low pressure UV light. Aliquots were taken from each sample over time and benzoic acid concentrations were analyzed using high performance liquid chromatography (HPLC). This data was then used to determine the initial reaction rate of •OH with the probe material.

As part of the bench testing, raw water samples were analyzed for similar parameters as in the preliminary testing to ascertain general water characteristics. The water samples were taken from a well representing the most challenging water quality as compared to the remaining wells. For these experiments, the water was spiked with high concentrations of 1,4-dioxane (300 and 3000 µg/L) and chloride (80 mg/L). The dioxane was spiked to represent possible elevated concentrations in the future. The end result was testing of a water sample that represented the "worst case" scenario for treatment.

Samples of raw water were collected and sent to each supplier for testing and analysis. Tests were conducted on water spiked with 300 µg/L dioxane and a higher 3000 µg/L spiked concentration of dioxane.

Pilot Tests

The following presents the general approach to the experimental plan:

1. Pre-chlorination
2. Filtration
3. Post-Filtration AOP

Pre-chlorination

The filter supplier recommended a target chlorine residual of 0.1 mg/L in the filter effluent. A low residual indicates that the dose is just over the required amount for contact time for oxidation of metals as well as to rejuvenate the catalytic filter media. Higher doses would be wasteful; especially since AOP systems utilizing hydrogen peroxide would have to compensate by increasing the H_2O_2 applied dosage for the excess demand exerted by the chlorine.

The filter supplier (Napier Reid) recommended a five-minute contact time and a design filtration rate of 12 m/hr. Chlorine contact was provided dosing the appropriate amount of chlorine just upstream of 4 reactors, in series. The dose was flow-paced, and was automatically adjusted according to the filter effluent chlorine residual. During sampling, chlorine residual levels were confirmed using a portable HACH kit. In all cases, residual concentrations were similar, and where there were discrepancies, the online monitor was adjusted.

The pilot filters had a maximum filtration rate of approximately 18 m/hr (equivalent to 87.5 L/min). The corresponding contact time at the maximum filtration rate of 18 m/hr was 4.3 minutes.

Filtration

Prior to the shutdown of the plant, a filter upgrade was planned, including the replacement of existing conventional greensand media with Napier Reid's high-performance MD-80 catalytic oxidative media. This new media was used for the pilot filter, sized and configured as per the filter supplier's recommendation. One 610 mm

(24 inch) pressure filter capable of filtering 15 US gpm (57 Lpm) was used. The media configuration is described in the Table 1.

Table 1. Filter Media Characteristics

Media Type	Effective Size	Depth
Anthracite	0.8 to 1.0 mm	300 mm
MD-80 Catalytic media	20 x 40 mesh	500 mm
Garnet sand	1.2 to 1.4 mm	300 mm

Advanced Oxidation

The UV/H_2O_2 system was supplied by Trojan Technologies Inc., which consisted of a UV Pilot Unit, SWIFT-SC: Model B08, based on the Trojan SWIFT SC UV system. The O_3/H_2O_2 system was the HiPOx unit, supplied by Applied Process Technologies (APT). Purifics ES Inc. provided the mobile Photo-Cat® system, a trailer-mounted UV/TiO_2 pilot plant, for the study.

All three AOP systems were used in parallel, receiving filtered water of the same quality for comparative purposes. The suppliers were responsible for optimizing and challenging their respective systems.

Results and Discussion

Bench-Scale Tests

Scavenging Potential

Scavenging potential is important to assess in an advanced oxidation application because it greatly affects the efficiency of an AOP. Several factors contribute to scavenging potential, some of which include alkalinity, chloride, and organic matter present in the water.

The scavenging potential, represented by ks, was determined to be 1.1×10^7 s^{-1}. This value is likely due primarily to bicarbonate, chloride, and natural organic matter. By using literature values reported for the reaction between hydroxyl radicals and these components we can estimate the relative contribution of each to the overall scavenging of the radicals. These reported reaction rate constants are (Buxton *et al.*, 1988; Grigor'ev *et al.*, 1987; Wang *et al.*, 2000):

Bicarbonate: $k = 8.5 \times 10^6 \ s^{-1}$
Chloride: $k = 3 \times 10^9 \ s^{-1}$
Organics: $k = 2.8 \times 10^8 \ s^{-1}$

The value shown for "organics" represents a typical value reported for natural organic matter in drinking water sources. The value shown for chloride does not take into account a reported reverse reaction in which the intermediate compound formed upon the scavenging of the hydroxyl radical by chloride decomposes and releases the radical.

Nevertheless, given the bicarbonate, chloride, and TOC of the groundwater, it can be estimated by simple chemical competition kinetics (equations not shown) that the bicarbonate and the organic matter contribute overall to less than 2% of the measured scavenging potential. The majority is predicted to be due to chloride.

Raw Water Characteristics

The results depicting general water quality parameters are shown in Table 2 below.

Table 2. Raw Water Characteristics

PARAMETER	RANGE	WELL TESTED
pH	6.62 - 7.29	6.62 – 7.09
Alkalinity (mg/L as $CaCO_3$)	201 – 352	329 - 338
UVT (%)	87 – 95	87 - 89
Chloride (mg/L)	7 – 244	158 – 160
Bromide (μg/L)	10 - 268	190 - 268
Nitrate (mg/L)	< 0.1 – 0.18	< 0.1
Nitrite (mg/L)	< 0.1	< 0.1
TOC (mg/L)	0.6 – 2.35	1.96 – 2.35
DOC (mg/L)	0.6 – 2.2	1.7 – 2.2
Iron (mg/L)	0.052 – 2.63	0.943 – 1.09
Manganese (mg/L)	0.300 – 0.654	0.421 – 0.432
1,4-Dioxane (μg/L)	Up to 300	Up to 300

Dioxane Reduction

Samples of raw water were collected and sent to Trojan Technologies for testing and analysis. Table 3 below shows the results of the bench-scale testing performed with their bench-scale UV/H_2O_2 AOP system. A collimated beam apparatus was used to perform the tests on the 300 μg/L dioxane water, while a medium pressure flow-through reactor was used to test the higher 3000 μg/L spiked concentration of dioxane.

Table 3. 1,4-Dioxane Destruction with UV/H_2O_2

Sample Spike (µg/L)	Initial Dioxane Conc. (µg/L)	Target Level (µg/L)	Final Dioxane Conc. (µg/L)	UVT_{254} (%/cm)
300	367.3	<5	3.9	90.4
300	367.3	≤ 20	12.6	94.3
3000	3626.9	≤ 20	16.6	95.9
3000	3626.9	≤ 5	1.8	95.8

Samples of raw water were collected and spiked with 300 µg/L 1,4-dioxane and 80 mg/L chloride and shipped to APT for testing using O_3/H_2O_2 technology. Bench-scale tests were performed using a total of five individual runs per sample. Three (3) tests employed low, medium, and high ozone dosages and a constant hydrogen peroxide molar ratio in order to develop a destruction curve (Figure 1). Two tests were operated at a high ozone dosage but at moderate and high hydrogen peroxide molar ratios. During the testing, analytical samples were collected at the beginning and end of each run and sent to an outside laboratory for analysis.

Figure 1 depicts the O_3/H_2O_2 system's destruction characteristics, which can be used to model the design and performance of the final system. It should be noted that one of the points (SP-18 at MR=4.3) was excluded in developing the predictive model due to an obvious analytical error. With that point removed, the resulting destruction curve is close to expectations.

Samples of raw water were collected and spiked with 300 µg/L 1,4-dioxane and 80 mg/L chloride and also shipped to Purifics for testing using UV/TiO_2 technology. Bench-scale tests were performed using the Purifics' Photo-Cat® system (UV/TiO_2). This system was able to reduce the 1,4-dioxane down to 8 µg/L from 3000 µg/L. This is shown in Figure 2 below.

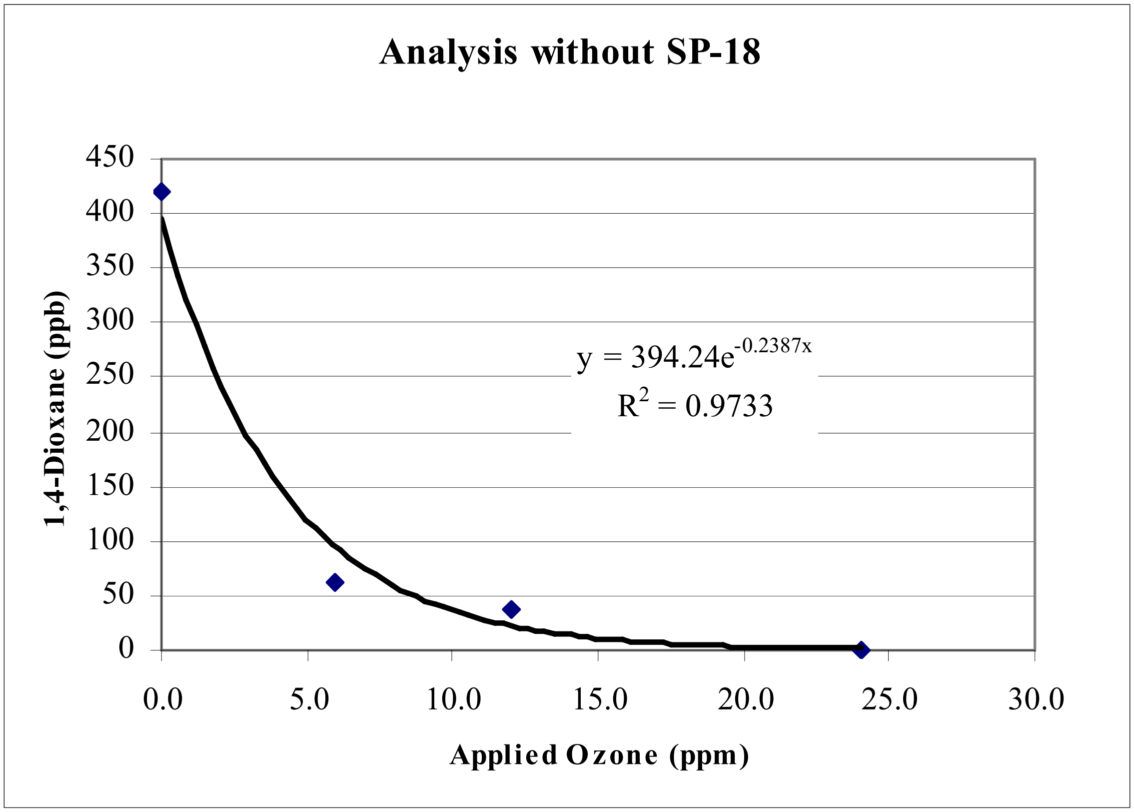

Figure 1. 1,4-Dioxane Reduction with O_3/H_2O_2

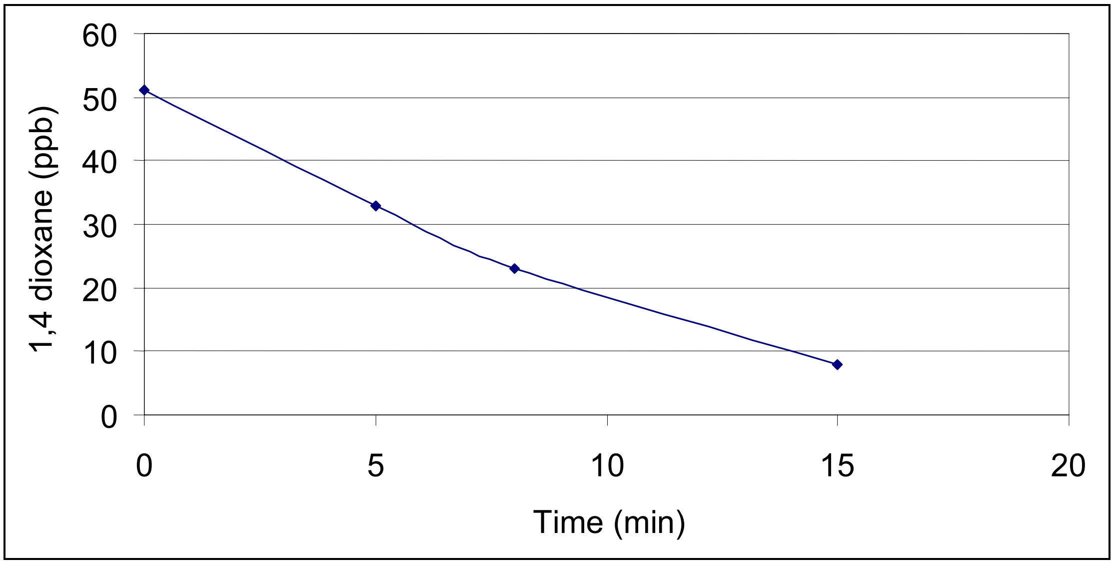

Figure 2. 1,4-Dioxane Reduction with UV/TiO_2

Pilot Testing

Filtration

When the filters were operated at the maximum rates (18 m/hr), run times were typically less than 24 hours. Lower filtration rates (12 m/hr) resulted in run times of nearly 72 hours.

The metals were sampled approximately in the middle of the run and at the end of each filter run when filter efficacy may have been hindered. Filter runs were terminated based on one of the following criteria:

- Iron level above 0.3 mg/L
- Differential pressure (headloss) above 5 psi
- Turbidity (0.2 NTU or greater)

Figure 3 shows the iron removal through the filter at various filtration rates. As expected, the results show deterioration in iron removal as the filter run progresses, and as filtration rates increase. According to the graph, the effluent met the aesthetic objective level of 0.3 mg/L at filtration rates below 17 m/h. This deterioration may also be attributed to a shorter contact time (approx 8.4 min at 9.3 m/h vs. 4.3 min at 18.1 m/h) between the oxidant (chlorine) and the iron, since the flow through the contact chambers was increased. In contrast, manganese removal was not impacted even with increased filtration rates (Figure 4), consistently meeting the aesthetic objective of 0.05 mg/L. Manganese requires much longer contact times for oxidation; therefore a difference of a few minutes would not greatly impact oxidation prior to filtration.

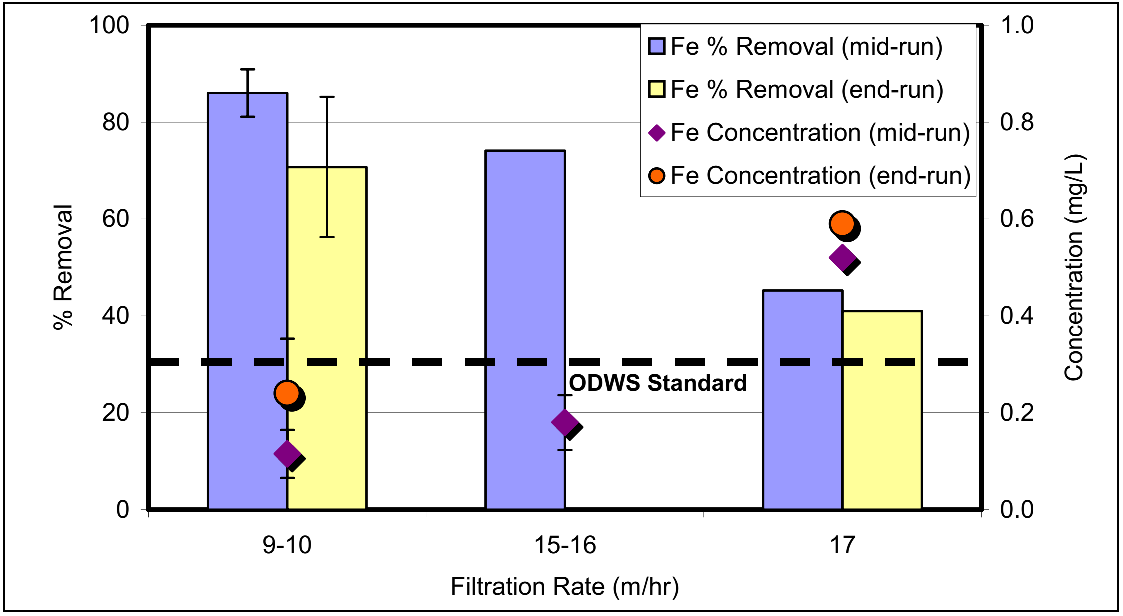

Figure 3. Iron Removal at Various Filtration Rates

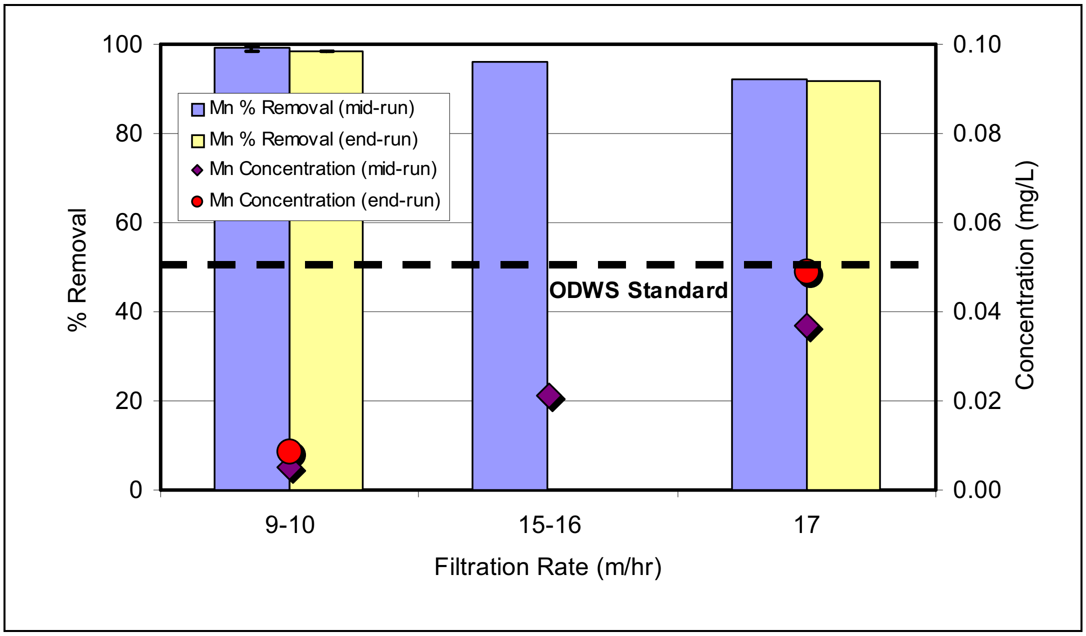

Figure 4. Manganese Removal at Various Filtration Rates

Another objective of testing filtration in this study was to assess any additional benefit of enhancing UVT and/or removal of radical scavengers in order to improve AOP performance. Several water quality parameters were monitored before and after the filter to determine what impact filtration had on turbidity, UVT, metals (namely iron and manganese), and radical scavengers.

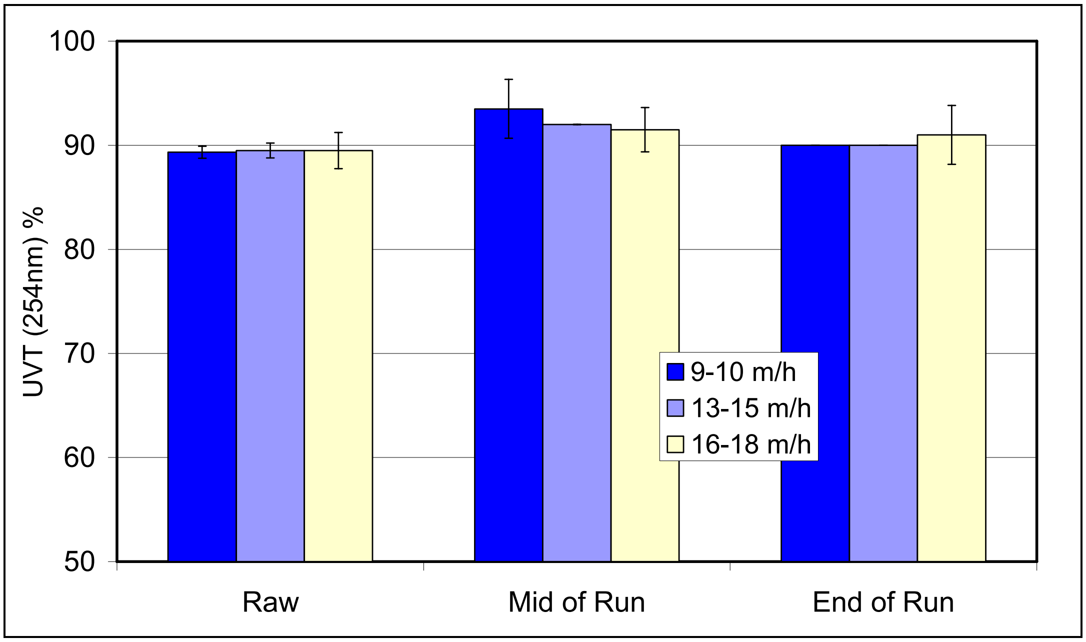

Figure 5. Impact of Filtration on UVT

During the study, radical scavengers such as alkalinity and chloride did not decrease through the filtration step. Table 4 shows the raw and filtered values of both scavengers.

Table 4. Impact of Filtration on Radical Scavengers

Parameter	Well Source	Raw Water (mg/L)	Filter Effluent (mg/L)
Alkalinity	Well A	348 +/- 9	350 +/- 9
Chloride	Well A	267 +/- 4	270 +/- 6
Alkalinity	Well B	273 +/- 8	283 +/- 8
Chloride	Well B	101 +/- 3	104 +/- 3

Turbidity profiles were generated for each filter run. Figure 6 shows a turbidity profile with the corresponding flow trend. The filter media consisting of anthracite, MD-80, and garnet sand helped remove some turbidity from the raw water. It was observed that most of the turbidity was due to metal precipitates, which often collected in the turbidimeters and may have caused higher than actual turbidity readings on some occasions.

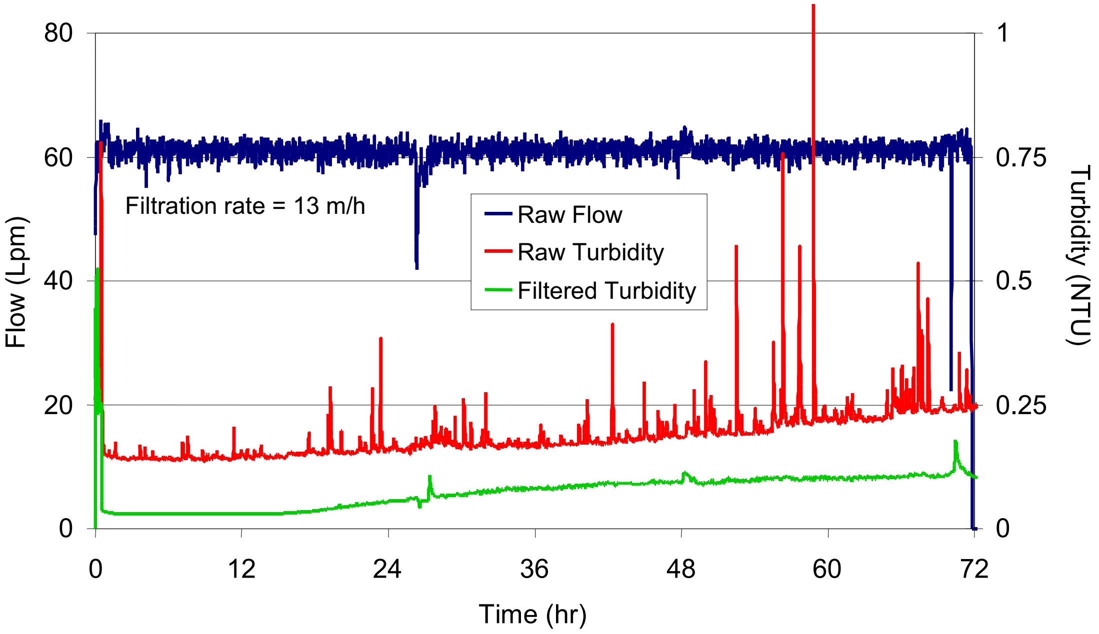

Figure 6. Typical Flow and Turbidity Profile

Dioxane Reduction

Since all three AOP technologies tested at bench-scale were able to reduce 1,4-dioxane to target levels, all three were tested during the piloting phase. At pilot-scale, each of the AOP systems was able to treat 1,4-dioxane to the target level of 10 µg/L when their systems were optimized. The O_3/H_2O_2 system faced a different challenge compared to the UV-based AOPs. The high bromide levels in the raw water during preliminary sampling raised a concern with using a treatment involving ozonation, with the potential to form bromate, an unwanted by-product of ozonation. The O_3/H_2O_2 system showed it is capable of destroying 1,4-dioxane from this well water without producing measurable levels of bromate.

It is difficult to graph the individual performance of each AOP due to the influence of raw water parameters on performance. The operating conditions were not always optimized but rather the units were sometimes stressed to evaluate their performance during challenging conditions. Comparison in system performance was assessed when two or more units were either run simultaneously, or operated with the same upstream filtration conditions. Raw water dioxane levels ranged from 47 to 151 µg/L. The larger than expected range is due to the use of two laboratories utilizing different methods for 1,4-dioxane analysis, and the difference in reported results is likely attributed to this difference in analytical methodology. Despite the variations in methodology, precision and accuracy, both methods have been based on USEPA approved standard methods and are considered appropriate for this application. One observation was made in the dioxane levels reported; lower concentrations (< 10 µg/L) were more likely to be similar between the two laboratories, as compared to higher concentrations. As mentioned previously, the proof testing of the two labs showed 100% and 80% recovery at low concentrations. Higher concentrations resulted in 95% and 106% recovery.

The following figure shows pilot trials where 2 or 3 AOPs were operated simultaneously, receiving the same influent water supply. Although Figure 7 may suggest one technology is better than another, it is important to note that not all AOPs for a given run may have been optimized (i.e. # lamps on, flow rates, chemical dosing). The key point of the pilot study is that all AOPs tested in this study were able to successfully meet the low target dioxane levels at some point during the study.

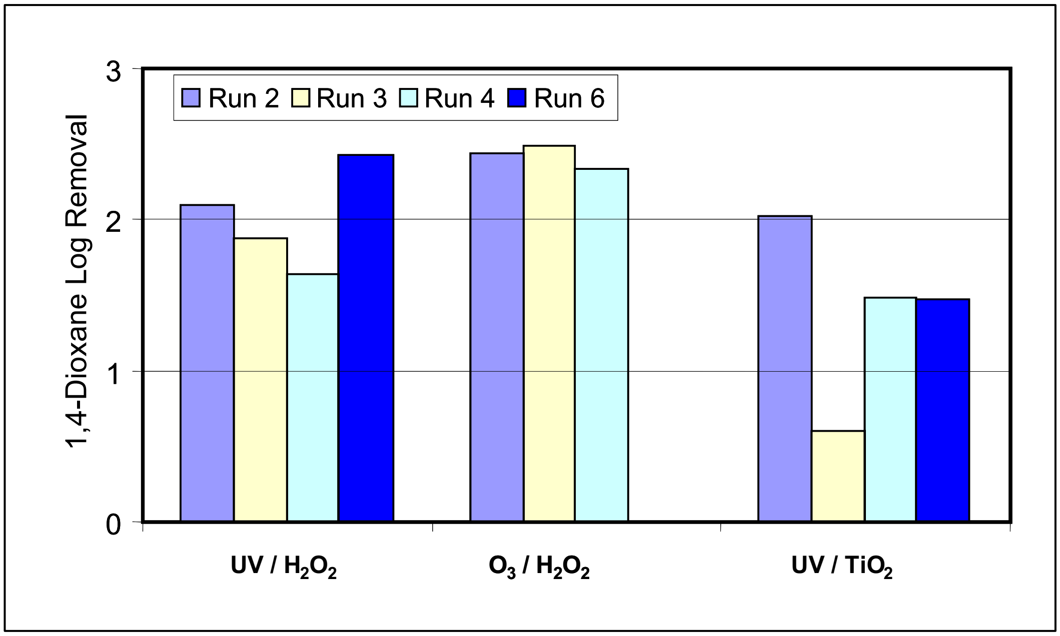

Figure 7. Comparison of 1,4-Dioxane Destruction

Other Considerations

Although the purpose of this study was to assess the performance and ability of each AOP to reduce 1,4-dioxane to target levels, other considerations were also realized. The UV/ process has some drawbacks in that UV converts little H_2O_2 to hydroxyl radicals. The addition of hydrogen peroxide means there is a need to quench leftover H_2O_2, whether chemically or with catalytic means (GAC contactors). Furthermore, unlike the other two AOPs, this technology is sensitive to UVT and like all AOPs, it is sensitive to radical scavengers like bicarbonate and organics. Lamp scaling issues due to hardness and the presence of metals in the water also interfere with the performance of a UV/H_2O_2 system. The advantages of this technology include its full-scale potable water experience, which may be a significant factor for some water providers. Also, this technology is easy to integrate into a treatment process, particularly an existing treatment process, as it has a small footprint.

The reaction between ozone and hydrogen peroxide is theoretically a very efficient way to produce hydroxyl radicals, since the reaction occurs in a 1:1 molar ratio to form 1 mole of the radicals. This is in contrast to other processes such as UV/H_2O_2 where only a small fraction of the UV light directed at the water is adsorbed by the H_2O_2 to produce radicals. Although it may be more efficient, the O_3/H_2O_2 system was more complex compared to the other AOPs tested in this study. The addition of peroxide, as with the UV/H_2O_2 system, means it also needs quenching of leftover peroxide prior to distribution. Finally, the formation of bromate as a by-product in the water needs to be monitored carefully when bromide is present in the water being treated.

A major benefit of the UV/TiO_2 technology is that no chemicals are consumed in the process. Unlike the other two AOPs, hydrogen peroxide is not required for this process, alleviating the need for a peroxide quenching system at the end of the treatment train. The lack of chemical use also alleviates the concern for disinfection by-product formation. Another benefit of this technology is the potential simultaneous removal of metals (iron and manganese), potentially eliminating the need for an iron/manganese filtration step. Furthermore, this technology is not sensitive to UVT in the water, as with the UV/H_2O_2 system. It is the reaction with titanium dioxide with the contaminant, not the UV transmittance that is key in this process. One major drawback of this technology is the lack of NSF 60 or 61 certification. These standards require that all chemicals used in the treatment process and all materials contacting the water shall meet both the American Water Works Association (AWWA) quality criteria as set out in AWWA standards and the American National Standards Institute (ANSI) safety criteria as set out in ANSI standard NSF/60 or NSF/61. Finally, the lack of full-scale potable water experience is also a challenge for this technology as many municipal clients hesitate to use technologies that have not been used in potable water before.

Conclusions

All three advanced oxidation systems, UV/H_2O_2, O_3/H_2O_2, and UV/TiO_2 successfully reduced the 1,4-dioxane concentrations to target levels, even when spiked during bench-scale tests to the high 3000 µg/L dioxane levels.

The recommendation for the most appropriate technology was based on the following criteria: full-scale technology experience, experience in treating 1,4-dioxane in water, AOP treatment performance, compliance with Ontario drinking water regulations, capital and life-cycle cost estimates, ease of operations and maintenance, constructability – delivery, schedule, footprint, reliability, sustainability, compatibility with overall water treatment process, and ancillary systems – chemical, power, residuals. Based on these criteria, the UV/H_2O_2 process was selected for full-scale implementation.

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