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ENVIRONMENTALLY FRIENDLY METHODS OF WATER DISINFECTION: THE CHEMISTRY OF ALTERNATIVE DISINFECTANTS

GILBERT GORDON AND BERNARD BUBNIS

Department of Chemistry and Biochemistry
Miami University, Oxford, Ohio USA
Tel: 513-529-3336
Fax: 513-523-0005
E-mail: gordong@MUOHIO.edu

ABSTRACT

The risk of disease from microbiological organisms far surpasses any chemical risk associated with water treatment by chemical oxidation. *Giardia lamblia* and *Cryptosporidium parvum*, common microbiological contaminants, sometimes have fatal consequences to individuals with weak immune systems. Because effective environmentally friendly oxidants are available and accessible for treating drinking water, utilities throughout the industrialized world are investigating alternative disinfection/oxidation practices. Chlorine dioxide and ozone are frequently used to remove taste and odor problems, color and to inactivate problem microbiological species. To understand the unique value of ozone and chlorine dioxide in water treatment, one must start with the chemistry. © 2000 Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

Legislation in the United States (USEPA, 1994a, 1994b) is mandating that drinking water utilities implement disinfection practices that balance the risks associated with chemical oxidation against the health risks arising from the presence of problem microbiological organisms (e.g. *Giardia* and *Cryptosporidium*). For many years the addition of chlorine to drinking water was thought to be sufficient treatment. However, chlorine can readily react with organics in the water to form chlorinated by-products (e.g. trihalomethanes, THMs). Trihalomethanes are currently regulated in the United States under the Safe Drinking Water Act (Safe Drinking Water Act Amendments, 1986) (SDWA). The THM maximum contaminant level (MCL) is 100 µg/L. In the near future, the MCL will be lowered to 80 µg/L. This means that many drinking water utilities will have to make adjustments in their current treatment practices.

It is widely recognized that the health risks from microbiological agents (*i.e.* bacteria, viruses, parasites) far outweigh the chemical risks associated with chlorine treatment. This is why chlorine is (and will probably continue to be) the most widely applied chemical oxidant. However, Table 1 shows that chlorine treatment is not a very effective biocide against *Giardia* and *Cryptosporidium* when compared to alternative oxidants such as ozone (O_3) and chlorine dioxide (ClO_2) (American Water Works Association, 1991).

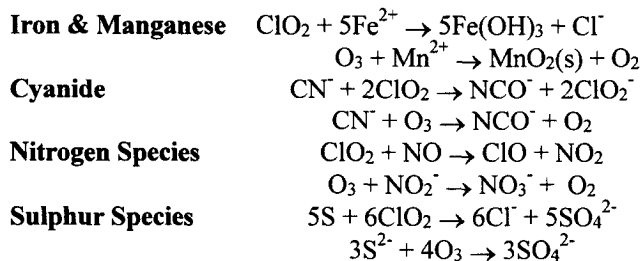
Table 1. Relative $C \times T$

	Cl_2	O_3	ClO_2
<i>E. coli</i>	0.03 - 0.05	0.02	0.4 - 0.8
rotavirus	0.01 - 0.05	0.01 - 0.06	0.2 - 2
<i>G. Lambliia</i>	47 - >150	0.5 - 0.6	26
<i>Cryptosporidium</i>	7,200	5 - 10	78

2. ENVIRONMENTALLY FRIENDLY ALTERNATIVE OXIDANTS

Chlorine dioxide is a strong oxidant that reacts by means of a one-electron transfer mechanism. In contrast, O_3 can react by either a one- or two-electron process depending on pH. An important distinction between O_3 and ClO_2 compared to chlorine is that O_3 and ClO_2 do not chlorinate. Thus, THMs are not readily formed as a by-product of treatment. The selective and highly efficient nature of O_3 and ClO_2 oxidation is used by many industries to solve common water treatment problems such as the disinfection of *Giardia* and *Cryptosporidium*, pre-oxidation as a means of removing iron and manganese in raw water, removal of taste, odor, and color from waters containing a high concentration of humic matter and in some cases, O_3 and ClO_2 are used for post-disinfection.

A major reason for the appeal of alternative oxidants such as O_3 and ClO_2 is that they can be used to treat a wide range of environmental issues as shown below (neglecting H_2O and H^+/OH^-):



In the drinking water industry, alternative oxidants are frequently the subject of speculation and myth (Masschelein, 1999). For example, ClO_2 is an outstanding alternative to Cl_2 . However, the chemical and patent literature continually makes reference to misleading information that is confusing and not true. Stabilized ClO_2 is a good example. Stabilized ClO_2 does not exist, however "buffered" $NaClO_2$ solutions are quite common. The bad news is that these myths about alternative oxidants persist in the scientific literature.

Many utilities throughout the world will continue to use chlorine for disinfection because of its simplicity. To reduce the presence of THM precursors prior to chlorination, a multiple barrier approach should be considered. The use of filters, improvements in the clarification process or the implementation of preoxidation (*e.g.* O_3 , ClO_2 , or chloramines) can improve chlorine oxidation. Liquid bleach ($NaOCl$) is a good alternative to Cl_2 gas at many utilities. $NaOCl$ above pH 11 decomposes slowly ($t_{1/2} > 60$ days). Thus, long-term storage is an

advantage for small utilities. If THM problems persist, in some cases changing the point of chlorination or the use of activated carbon filtering should be considered.

Utilities using liquid bleach (chlorine) should develop a set of minimum specifications for delivered bleach from their supplier (Gordon et al., 1994). For example, the minimum specifications for 9.5 Wt% bleach should include:

- pH greater than 12
- Ni^{2+} and Cu^{2+} concentrations less than 0.1 mg/L
- specific gravity greater than 1.14
- ClO_3^- concentration less than 1.5 g/L
- delivery within 1 week of manufacture

In the United States, Europe and Japan, ozone is rapidly becoming the "disinfectant of choice" when *cryptosporidium* or other resistant microbial species are present in the raw water. At pH <7, ozone does not react with water and is present as molecular O_3 (Kawamura, 1932; Adler and Hill, 1950). However, as the pH is elevated, spontaneous decomposition occurs through a variety of steps to ultimately produce reactive free radicals, such as the hydroxyl radical (OH). Many utilities in the United States are investigating the possibility of using ozone for disinfection to satisfy new drinking water regulations. Because the cost of ozone continues to decrease, there is a likelihood that many drinking water utilities will choose ozone over other alternative oxidants.

3. CONCLUSIONS

Alternative oxidants are widely used throughout the world for drinking water treatment for the following reasons:

- Environmentally friendly
- Potential to lower unwanted by-products
- Effectively "disinfect" problem microbes
- Technologies are readily available
- Low potential for "chemical" risk
- Higher quality drinking water

Their efficient application requires a chemical understanding of the oxidation process. With the aid of a complete "chemical model", sensible and environmentally friendly decisions can be made with respect to applying oxidants in water treatment.

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