Technical note

Assessment of a chlorine dioxide proprietary product for water and wastewater disinfection

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Abstract

Chlorine on its own is adequate for many, if not most, potable water pre-oxidation and disinfection systems at plants where the application is straightforward. Similarly, most wastewater plants can be disinfected by chlorine in one of its commercially available forms. However, when more intense pre-oxidation is required or significant iron or manganese is present in a potable supply, the use of alternative disinfectants is often preferable. Similarly, when secondary problems are present in wastewater effluent, such as high ammonia, a stronger oxidant may be preferable. Hitherto, the use of stronger oxidants has been limited to large works due to the complexity of the operational processes required. Recently, the use of ozone has spread to smaller works as new developments in equipment have become available. However, chlorine dioxide has not been used in small works until now. This paper provides details regarding a product which is simply dissolved in water in tablet or granular form and generates chlorine dioxide on solution in water. The solution is stable over weeks or even months and can be used for disinfection and or pre-oxidation purposes. The chemical was assessed in a series of tests. The performance of the chlorine dioxide product was compared against sodium hypochlorite, for different water types. The reduction in microbial counts was monitored in a secondary effluent sample and a high-ammonia secondary effluent sample. The oxidation ability in a high iron and manganese water was also assessed. A cost assessment was carried out and compared to the use of sodium hypochlorite. Other factors such as safety ease of use, and storage requirements are discussed.

Keywords: chlorine, chlorine dioxide, oxidant, iron, manganese

INTRODUCTION

The treatment of water and wastewater is physical, chemical and biological in nature. The object of the process is to remove contaminants and produce water which is suitable for potable use, or an effluent of a quality that can be discharged into the environment. As part of the process, pre-oxidation may be necessary when treating potable water to oxidise organic compounds as well as iron or manganese which may exist in a reduced form in many borehole waters and impounded supplies. The oxidant used is invariably also a strong disinfectant and can also render the water bacteriologically safe. Disinfection of a wastewater effluent is an important final stage of wastewater treatment. It plays a vital role in the reduction of waterborne diseases and the destruction/sterilisation of pathogens. In summary, disinfection reduces the number of microorganisms in the water to be discharged back into the environment in order to provide for the later uses of the water for drinking, bathing, or irrigation.

Disinfection may be obtained by chemical, physical or biological methods. The chemical method of chlorination is the most common form of disinfection used. Historically, small wastewater works may use calcium hypochlorite tablets or the more familiar liquid sodium hypochlorite (NaOCl) (usually approximately 13% chlorine) as a chemical disinfectant. Chlorine, whether by gas or hypochlorite addition, is by far the most common method of disinfection and has saved millions of people from waterborne disease over the past 100 years.

However, chlorine has a number of shortcomings under certain circumstances. When used for pre-oxidation in potable water treatment, it can give rise to trihalomethanes which are carcinogenic. It is also slow to oxidise manganese which can then pass through the works and contaminate the distribution system (Freese, 2008). Also, when chlorine is applied to wastewater effluent which has high ammonia concentrations, it is relatively ineffective within the time frame between dosage and discharge into the environment (Freese, 2008). Chlorine dioxide (ClO_2) is an alternative chemical which may also be used in the treatment of water and wastewater as an oxidant and disinfectant.

Iron (Fe) and manganese (Mn) in a wastewater effluent are considered as microelements. However, if they are in sufficient concentrations, they do have a toxic impact on the receiving environment. To reduce the impact, soluble Fe^{2+} and Mn^{2+} are oxidised to their insoluble forms of Fe^{3+} and Mn^{4+}, which may be filtered prior to discharge.

This paper reports on an investigation carried out on a patented chlorine dioxide product. This product is produced as a tablet or granular product which, when added to an appropriate volume of water, generates a solution which contains approximately 0.2% chlorine dioxide. It is not readily possible to assess the effect of a disinfectant on potable supplies when the bacterial counts may be too low to draw conclusions. Tests were therefore carried out to assess the effect on microbial counts, on a wastewater effluent and a high-ammonia wastewater effluent,

This paper was originally presented at the 2012 Water Institute of Southern Africa (WISA) Biennial Conference, Cape Town, 6–10 May 2012.

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http://dx.doi.org/10.4314/wsa.v39i3.5
Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 39 No 3 WISA 2012 Special Edition 2013
ISSN 1816-7950 (On-line) = Water SA Vol. 39 No 3 WISA 2012 Special Edition 2013

and to assess the ability of the chlorine dioxide product to act as an oxidant on a wastewater effluent with high iron and manganese concentrations.

MATERIALS AND METHODS

Secondary wastewater effluent from a clarifier at an activated sludge plant was used as the base sample. The patented chlorine dioxide product was in the form of a tablet which was dissolved in water to obtain a solution which matured on standing. A ±19.7 (nominal 20) g tablet was dissolved in 1 000 mℓ deionised water. Sodium hypochlorite was prepared from a commercial solution. This was standardised and suitably diluted to obtain the desired concentration of chlorine for the dosing range required. Both the chlorine dioxide and the sodium hypochlorite solutions were standardised daily before use (Leopold et al., 2009).

The dosage trials were carried out to assess the relative effectiveness of the addition of chlorine dioxide (ClO_2) and sodium hypochlorite (NaOCl) to the wastewater effluent, at the concentrations of 0 mg/ℓ (blank), 1 mg/ℓ, 1.5 mg/ℓ 2 mg/ℓ, 3 mg/ℓ, 5 mg/ℓ and 8 mg/ℓ (Freese et al., 2004).

In all *E. coli* reduction tests, 500 mℓ aliquots of sample were used. After addition of the disinfectant, the samples were stirred for 2 min and allowed to stand for 30 min, prior to measurements.

To test and compare the iron and manganese removal ability of the two oxidants, the following test procedure was followed:

Spiked solutions of iron and manganese were prepared using secondary effluent, with suitable additions of ferrous and/or manganous sulphate solutions (weighed and standardised) (Freese et al., 2004). The procedure was:

- Make up 500 mℓ aliquots of water with about 2 mg/ℓ iron, and 1 mg/ℓ manganese in 6 beakers.
- Add 0; 1; 2; 4; 6 mg/ℓ sodium hypochlorite or patented chlorine dioxide product solution.
- Rapidly mix for about 30 s and add 2.5 mg/ℓ U3500 polyelectrolyte solution; then rapidly mix for another 90 s.
- Slowly mix for 5 min.
- Stop mixing and immediately filter through GF/C paper.
- Read iron and manganese on filtrate immediately.

Stability

Fresh solutions of sodium hypochlorite were prepared as required. The stability of the patented chlorine dioxide product in solution was determined by reading the concentration of the ClO_2 solution over a series of weeks and calibrating accordingly.

RESULTS AND DISCUSSION

Stability of the chlorine dioxide product

The results shown in Fig. 1 and Fig. 2 indicate that the product is at its most active 1 or 2 days after it is prepared; however, it remains stable for up to approximately 6 weeks in solution.

Comparison between *E. coli* reduction using chlorine dioxide and sodium hypochlorite on the base effluent and high-ammonia effluent

Results from tests carried out as per the method above are presented in Figs. 3 and 4.

Microbial counts in the water types tested were reduced by both disinfectants. In the 'base' effluent, the reduction in

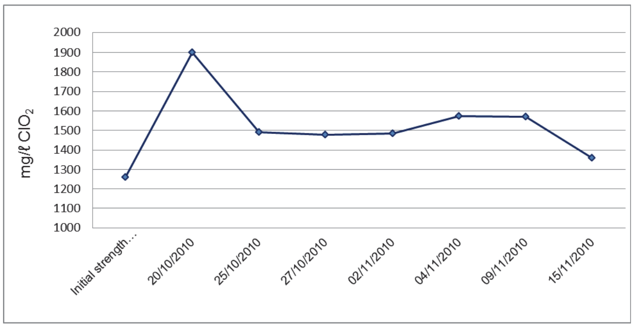

Figure 1
Stability of the chlorine dioxide product over a period of 5 weeks

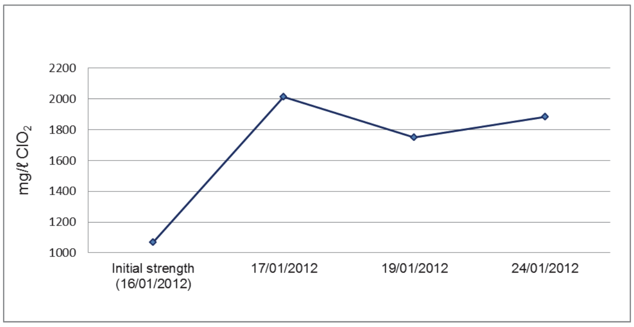

Figure 2
Stability of the chlorine dioxide product recorded over a period of 1 week

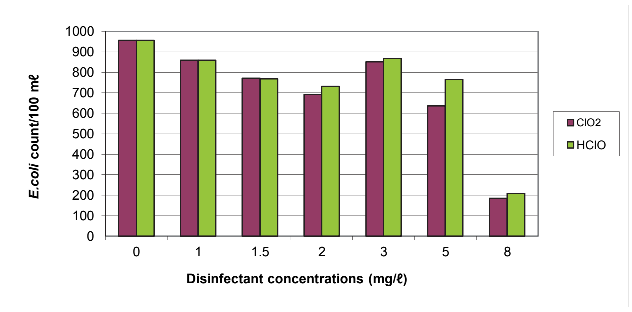

Figure 3
E. coli count comparison for the 'base' effluent sample

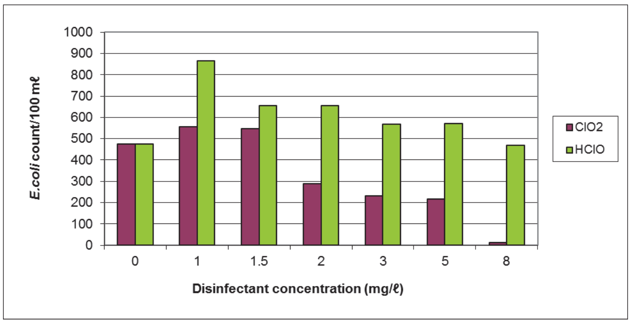

Figure 4
E. coli count comparison for the high-ammonia effluent sample

E. coli detected seemed to be almost identical, whether chlorine or patented chlorine dioxide product was used.

On high-ammonia effluents and as expected, the use of the chlorine dioxide product seems to have a better response and

http://dx.doi.org/10.4314/wsa.v39i3.5
Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 39 No 3 WISA 2012 Special Edition 2013
ISSN 1816-7950 (On-line) = Water SA Vol. 39 No 3 WISA 2012 Special Edition 2013

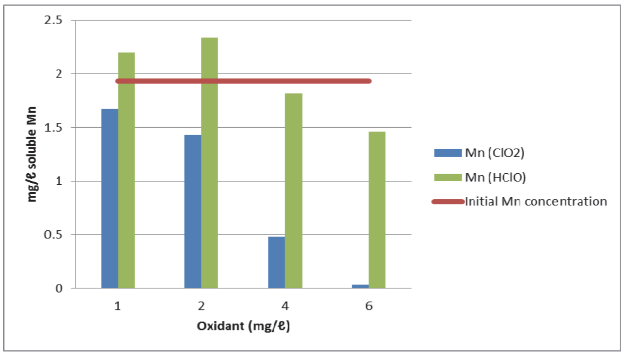

Figure 5
Manganese oxidation with patented chlorine dioxide product (ClO_2) and hypochlorite

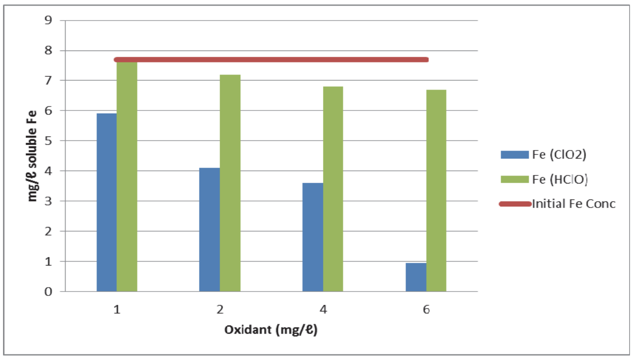

Figure 6
Iron oxidation with patented chlorine dioxide product (ClO_2) and hypochlorite

greater microbial kill rate. This confirms that ClO_2 retains its disinfecting ability as it does not react with ammonia to produce chloramines. It is well known that chlorine reacts with ammonia to form chloramines which have a greatly reduced disinfecting ability.

Oxidation of iron and manganese

Using the method described above the effect of the patented chlorine dioxide product on manganese was assessed, as shown in Tables 1 and 2.

TABLE 1
Effect of patented chlorine dioxide product on manganese

Concentration of patented chlorine dioxide product (ClO_2) added to 500 mℓ effluent	Mn (mg/ℓ)	pH
0	1.93	7.52
1	1.67	7.41
2	1.43	7.05
4	0.48	6.99
6	0.03	6.90

TABLE 2
Effect of NaOCl on manganese

Concentration of NaOCl added to 500 mℓ effluent	Mn (mg/ℓ)	pH
0	1.93	7.52
1	2.20	7.51
2	2.34	7.52
4	1.82	7.67
6	1.46	7.76

As can be seen, the expected pattern emerges: Chlorine dioxide rapidly oxidises both iron and manganese whereas chlorine is slow to oxidise iron and manganese (refer to Figs. 5 and 6).

Costs

For active ingredient in bulk (10% active), the patented chlorine dioxide product (ClO_2) granules cost about R3 000/kg (as at January 2012). On a single-household borehole at approx. 3 kℓ/d and 2.5 mg/ℓ dosage, the cost would be approx. R22.50/day. Sodium hypochlorite in 20 ℓ containers costs approx. R100/kg (as Cl_2). For a single-household borehole using approx. 3 kℓ/d at 5 mg/ℓ, the cost of NaOCl would be approx. R1.50/day. Hence, as at January 2012, the patented chlorine dioxide product (ClO_2) was significantly more expensive in usage than NaOCl.

CONCLUSION

The patented chlorine dioxide product (ClO_2) appears to have the advantages of chlorine dioxide over chlorine, i.e., effectiveness in high-ammonia effluents, and rapid oxidation of manganese. However, it does not appear to be a viable choice in view of its extremely high cost.

DISCLAIMER

The authors have no formal ties or working arrangements with any supplier of oxidants or disinfectants.

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http://dx.doi.org/10.4314/wsa.v39i3.5
Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 39 No 3 WISA 2012 Special Edition 2013
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