THE EFFECTIVENESS OF NOVEL CHLORINE DIOXIDE IN DRINKING WATER DISINFECTION

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: The presence of *E. coli* in drinking water is not very common, however drinking water polluted with *E. coli* can lead to infection and could cause serious illness. Water contamination can lead to adverse health effects, including gastrointestinal illness, reproductive problems, and neurological disorders. More than 200 diseases are derived from polluted water. The main objective of present research was to evaluate the effectiveness of novel chlorine dioxide for the inactivation of *E. coli* in drinking water. Chlorine dioxide is made of two compounds: liquid sodium chlorite and solid sodium-peroxodisulphate »in situ«. Chlorine dioxide composition is in accordance with water treatment regulation [1]. In this experiment, different concentrations of chlorine dioxide were added at different temperatures in order to determine the optimal conditions for *E. coli* removal from drinking water. Results showed that optimal dose is 0.2 mg/L of chlorine dioxide at room temperature, while the same dose was effective at increased temperatures at 30 °C and 40 °C. The contact time was less than 1 min.

KEYWORDS: drinking water disinfection, *E. coli*, chlorine dioxide

INTRODUCTION

Chlorine dioxide is known disinfectant agent. It is formed after the reaction between $NaClO_2$ and HCl. Beside chlorine dioxide also, NaCl is formed. The chlorine dioxide solution is not stable due to ClO_2 volatility. ClO_2 is very reactive in gaseous state therefore, it is used as aqueous solution [2]. Chlorine dioxide is more effective at lower temperature at certain contact time. Experiments showed that it is effective already after 1 min. Besides temperature, other factors such as pH, contact time and load of organic matter may influence the actual biocidal efficiency of ClO_2 [3] The same authors also found that the efficacy of ClO_2 is decreasing with increasing organic load. Factor that affect the efficiency is also pH value dependent, however in neutral range around pH = 7 the effectiveness does not change much as seen from Figure 1.

Chlorine dioxide is an effective compound capable of destroying bacteria, viruses, fungi and other cellular pathogens. It is used for drinking water disinfection as well as for disinfection of fruit in food industry. [4] Since chlorine dioxide destroys pathogens by eliminating vital proteins, the microorganisms cannot resist it by nor of their resistance mechanisms. [4]. Human and animal cells are not free from the cell-killing effect of chlorine dioxide, however, it is not harmful to the animal organism in low doses.

Table 1 presents the comparison between different disinfection products. Despite their efficacy, the main limit of the currently applied disinfectants (e.g. ozone, hydrogen peroxide, peracetic acid) is that they are toxic even at low concentrations [4]. It is seen that ClO_2 has some advantages regarding pH value and low production of disinfection byproducts (DBP). Most of DBP are formed by using chlorine, such as trihalomethanes (THM), haloacetic acid (HAAs), chloramines, etc.

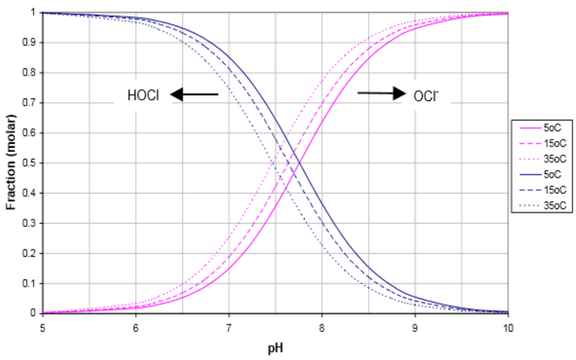

Figure 1. Effect of pH for the disinfection [5]

Table 1. Comparison of different disinfectant properties [6]

Chlorine	ClO_2	Ozone
residual	residual	-
High pH dependence	low pH dependence	middle pH dependence
DBP: THM, HAAs, etc.	chlorites	bromates
High bacteria inactivation	Very high bacteria inactivation	Very high bacteria inactivation

In drinking water, some coliform bacteria are present, among them *E. coli* in concentrations less than 50 CFU/100 mL. The amount of total organic halogen (TOCl) produced during ClO_2 oxidation was generally over ten times lower than that produced in chlorination [7] It was stated that humic acid (HA) could react with chlorine dioxide [7]. Phenolic moieties in humic acids were found to be the dominant fast-reacting precursors, responsible for the massive ClO_2^- formation in the first 5-min reaction if the concentration of humic acid was above 2 mg/L [7]. ClO_2 preferentially reacts with hydrophobic fractions of humic acids and decomposes high molecular weight fractions. Aromatic precursors (e.g., non-phenolic lignins or benzoquinones) contributed to ClO_2^- formation over longer reaction time (up to 24 h).

The aim of the work was to determine the efficiency of chlorine dioxide made in-situ on *Escherichia Coli* inhibition *(E. coli*). The bacteria waere chosen based on the fact that it is an indicator for water quality and the lifecycle of *E. coli* is longer than that of other bacteria [8]. A certain concentration of chlorine dioxide was added to constant number of *E. coli* colonies under different conditions, dependent on water temperature, chlorine dose and the concentration of organic compounds in water.

MATERIAL AND METHODS

MICROBIOLOGICAL EXPERIMENTS

The microbiological experiments were done in cooperation with National laboratory for health, environment and food (Maribor, Slovenia). Standard method ISO 9308-1 (2014) was used for determination of *E. coli*.

100 ml of water was filtered through 0.45 μm membranes. Membrane is placed on the surface of CCA medium and incubated at 36 ºC and 44 ºC for 24 h. The plates were examined for blue green colonies (indicating production of β-D-galactosidase positive and β-D-glucoronidase positive colonies have to be counted as *E. coli*. In the untreated water solution 200 colonies of *E. coli* were added. After different time units (1, 5, 10, 15 min) samples were taken and the number of colonies was measured as (CFU/100 mL).

PREPARATION OF CLO_2

The novelty of disinfection agent is that it could be prepared »in situ« very quickly and no safety precautions are necessary. Chlorine dioxide was made of two compounds: liquid sodium chlorite and solid sodium-peroxodisulphate »in situ«. Chlorine dioxide composition is in accordance with water treatment regulation [1]. In 100 mL of $NaClO_2$ 5,2 g $Na_2S_2O_8$ was dissolved. Such solution is suitable for disinfection of 1500 L of H_2O. The reaction is:

$$2\,NaClO_2 + Na_2S_2O_8 \rightarrow ClO_2 + 2\,Na_2SO_4 \qquad (1)$$

Producer Biostream (Zero, Germany) claims that the CLO_2 product does not depend of pH value.

CHEMICAL ANALYSES

Free and bound chlorine was determined with colorimetric DPD method, while the pH was measured using pH meter WTW, Germany. The absorbance (at 515 nm) using Agilent 8453 UV-Visible Spectrophotometer was measured after mixing regent with samples. Based on calibration curve the ClO_2 concentrations were determined. Excessive amount of NH_4Cl (21 mg) was added to another 10 mL of samples to stop free Cl_2 reactions before measurement of total chlorine concentrations. The total residual chlorine concentrations were also determined via absorbance at 515 nm after mixing total chlorine reagent with samples. The free chlorine level was calculated by subtracting the residual ClO_2 from the total residual chlorine. The LOD of ClO_2 and free chlorine were 40 and 10 μg/ L, respectively. The analyses were performed at room temperature.

RESULTS AND DISCUSSION

Chemical parameters (total chlorine, free chlorine and ClO_2) did not change if disinfectant was added. The pH, as well as the concentrations of total and free chlorine remained the same after the disinfection. The pH value of the water was between 7.4 and 7.5. The values of total and free chlorine were below 0.1 mg/L. The value of chlorine dioxide remained the same after the disinfection: if 0.2 mg/L of chlorine dioxide was added it remained 0.2 mg/L after disinfection.

To the initial water solution was spiked with 200 colonies of *E. coli* were added. For disinfection 0.2 mg/L ClO_2 was used. The results are presented in Table 2.

From Table 2 it can be seen that already after 1 min, the disinfection was efficient and total *E. coli* colonies were inactivated. The results are consistent with another study where inactivation was reached after 1 min [3]. From Figure 2 it is seen that no *E. coli* colonies were detected.

Table 2. The results after disinfection at 0.2 mg/L ClO_2 at 20 ºC

Time (min)	*E. coli* (CFU/100 mL), 20 ºC
0	200
0.5	100
1	0
5	0
10	0
15	0

Figure 2. Plate with no detected *E. coli*.

In the following experiments, the dose was lowered at 0.1 mg/L ClO_2. The results are presented in Table 3. As seen from Table 3 the results are the same as presented in Table 2 at higher dose. *E. coli* colonies were not totally removed by lower dose. The optimum dose 0.2 mg/L ClO_2 is in accordance with previously reported values [8]

Table 3. Results after disinfection at 0.1 mg/L ClO_2 at 20 ºC

Time (min)	*E. coli* (CFU/100 mL)
0	200
1	3
5	1
10	1
15	1

Therefore, the experiments were performed at higher temperature to prove if the temperature effects the disinfection efficiency. The results with the 0.2 mg/L ClO_2 at 30 and at 40 ºC are presented in Table 4.

Table 4. Results after disinfection at 0.2 mg/L ClO_2 at 30 ºC and 40 ºC

Time (min)	*E. coli* (CFU/100 mL), 30 ºC	*E. coli* (CFU/100 mL), 40 ºC
0	200	200
1	1	1
5	0	0
10	0	0
15	0	0

As seen from Table 4 the results are similar as with higher dose and lower temperature. Since the initial value of 200 colonies is very low, it cannot be assured that the same concentration of ClO_2 would provide efficient inactivation at higher initial CFU. In the next experiment the temperature was increased to 40 ºC. The results were identical to those presented in Table 4. However, due to cost limitation we could not perform experiment with higher temperatures (above 40 ºC).

The literature claims that organic pollution could affect the disinfection efficiency [5]. The experiment was performed with water spiked with 0.1 mg/L and 0.2 mg/L of humic acid. The dose of 0.2 mg/L ClO_2 was added to each sample. The results are presented in Table 5.

Table 5. Results after disinfection at 0.2 mg/L ClO_2 and 0.2 mg/L and 0.1 mg/L humic acid

Time (min)	*E. coli* (0.1 mg HA) (CFU/100 mL)	*E. coli* (0.2 mg HA) (CFU/100 mL)
0	200	200
1	0	0
5	0	0
10	0	0
15	0	0

The results showed that low doses of humic acid do not affect the disinfection in low concentrations at 0.2 mg/L. More studies should be done in higher concentration range of humic acid since it was reported in literature that concentration above 2 mg/L of humic acid have major effect on ClO_2 efficiency [6]

CONCLUSION

In this experiment, different concentrations of chlorine dioxide were added at different temperatures in order to determine the optimal conditions for *E. coli* removal from drinking water. Results showed that optimal dose is 0.2 mg/L of chlorine dioxide at room temperature. The same dose was effective at increased temperatures at 30 °C and 40 °C. The contact time for efficient disinfection was less than 1 min. Humic acid did not affect the disinfectant efficiency in concentrations below 0.2 mg/L.

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