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Impacts of water organic load on chlorine dioxide disinfection efficacy

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ABSTRACT

This study has examined the bactericidal effect of chlorine dioxide in untreated artificial and domestic wastewaters and secondary effluent of various organic loads. Results indicated that the inactivation of *Escherichia coli* in artificial wastewater was similar with that in real municipal wastewater. Among three waters, the bactericidal effect of chlorine dioxide was lowest in secondary effluent. The bacteria log inactivation increased by up to threefold when the COD concentration of raw wastewater was decreased by half. An unfavorable COD effect was also observed for the disinfection of secondary effluent. To explain the COD effect on bacteria inactivation, chlorine dioxide residuals were measured with time through each disinfection process. Results from statistical analyses have revealed that, in comparison to the correlations using *CT* values, the inactivation data can be better correlated with the ratio of COD to ClO_2 concentrations. The results of this study would be a useful guide for many municipalities and communities in determining chlorine dioxide dosages for water and wastewater disinfection systems.

1. Introduction

Disinfection of wastewater is important to protect surface and coastal water microbial quality [1]. Chlorine is one of the most commonly used biocide for water and wastewater disinfection due to its residual bactericidal effect and low cost [2]. Although chlorine is effective and economical for water treatment, its combination with organic compounds causes the generation of toxic and carcinogenic disinfection by-products [3]. Chlorine dioxide has been lately considered as an alternative to chlorine, since its reactions with organic or inorganic species in water do not usually lead to the formation of harmful toxic by-products [4]. In addition, chlorine dioxide (ClO_2) is more powerful than chlorine (Cl_2) as a bactericide for water treatment due to its higher oxidation capacity [5]. Chlorine dioxide accepts five electrons when reduced to chloride ion. Based on its molecular weight and number of electrons transferred, ClO_2 has approximately 263% available chlorine, which is more than 2.5 times the oxidizing capacity of chlorine in HOCl or Cl_2 [6].

The effectiveness of chlorine dioxide on killing pathogenic microorganisms depends on a number of factors including disinfectant dose, contact time, water temperature, pH, total suspended solids (TSS), and organic load (COD, DOC, NOM, etc.). Elevated water temperatures and disinfectant doses and longer contact times generally favor the inactivation of microorganisms by chlorine dioxide [7,8]. Chlorine dioxide effectively inactivates microorganisms within a wide range of pH 3–9 [9]. However, high concentrations of total suspended solids and organic contaminants in water significantly decrease the disinfection efficiency. TSS particles in water entrap some microorganisms, and so enable them survive through the disinfection process [10]. Some organic contaminants such as phenolic, sulfuric functional groups and amines in water react with chlorine dioxide, and as a result reduce the concentration of disinfectant residual [11]. The unfavorable influences of organic loads in terms of COD, DOC, TOC, or NOM on bacteria inactivation have been reported for the disinfection of wastewater and surface water with chlorine dioxide [12–17]. The decreased bactericidal effects have been attributed to the oxidation of chlorine dioxide by the organic contaminants in water and wastewater.

The elimination of total suspended solids and organic compounds appears to be an important step to achieve more successful water and wastewater disinfection with chlorine dioxide. However, the complete removal of TSS and organic contaminants from water may not always be feasible and applicable especially in places where the pollution discharge limits are high. For wastewaters with greater TSS and COD concentrations, the disinfection with chemical biocides such as chlorine, ozone, or chlorine dioxide is more complicated and a full disinfection can require high concentration of these disinfectants depending on the level of water contamination [18–20]. Therefore, an important question to be answered is what disinfectant dose should be used to obtain a complete bacteria inactivation during the disinfection of a specific wastewater. Although

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Nomenclature

C	disinfectant concentration (mg/L)
CFU	colony forming units
Cl_2	chlorine
ClO_2	chlorine dioxide
COD	chemical oxygen demand
CT	effective disinfectant dose (mg/L)
DBPs	disinfection by-products
DOC	dissolved organic carbon
E. coli	*Escherichia coli*
EC	electrical conductivity (μs/cm)
HCl	hydrochloric acid
HOCl	hypochlorous acid
k	inactivation rate constant (min^{-1})
$NaClO_2$	sodium chlorite
N	number of bacteria after disinfection (CFU/mL)
N^0	initial number of bacteria (CFU/mL)
NOM	natural organic matter
PBS	potassium buffer saline
T	contact time (min)
TC	total coliform
TSB	tryptic soy broth
TSS	total suspended solids

Greek letter

α	t-test confidence level (fraction)

there has been a broad research in the literature about the influence of organic and inorganic contaminants on the chlorine dioxide disinfection, a detailed study is still necessary to examine its impacts with more quantitative results.

The main goal of this study was to explore the subject of the influence of organic matter on chlorine dioxide disinfection efficiency. To explain the inactivation of microorganisms, disinfectant doses and residuals were evaluated along with wastewater COD concentrations. In this respect, killing effect of ClO_2 on *Escherichia coli* (*E. coli*) and total coliform (TC) inactivation were determined in artificial and real municipal wastewaters, and secondary effluent of various COD and disinfectant concentrations. The bacteria inactivation data were correlated using appropriate kinetic models.

2. Experimental

2.1. Preparation of wastewater samples

Artificial domestic wastewater was prepared by adding the amount of reagents given in Table 1 [21]. Artificial wastewater was diluted to obtain desired COD concentrations of target solutions. Raw wastewater and treated water samples were daily taken from the entrance and secondary clarifier effluent of KEPEZ Municipal Wastewater Treatment Plant in the city of Çanakkale, Turkey. As soon as a sample was brought to laboratory, its COD concentration was measured according to the standard methods of examination of water and wastewater [22]. The treated and untreated real wastewaters were also diluted to attain working COD initial concentrations. Physical and chemical characteristics of the wastewaters are presented in Table 2.

Disinfection experiments were conducted at 1, 2, and 3 mg/L of chlorine dioxide concentrations. For experiments made using untreated, artificial and real domestic wastewaters, COD concentrations were adjusted to 75, 150, and 300 mg/L, while for these performed using the secondary effluent COD concentrations were fixed to 12.5, 25, and 50 mg/L. The bactericidal efficacy of chlorine dioxide was examined based on log reductions in the number of bacteria.

Table 1
The receipt of artificial wastewater.

Components	Concentration (mg/L)
Casein	160
Meat extract	110
Urea	30
K_2HPO_4	28
$CaCl_2{\cdot}2H_2O$	4
$MgSO_4{\cdot}7H_2O$	2
NaCl	7

2.2. Source of bacteria and inoculation

E. coli and TC were selected as the representative indicator microorganisms to examine the bactericidal efficacy of chlorine dioxide in diluted municipal wastewater samples. For experiments made using artificial wastewater, a pure culture of *E. coli* (ATCC 8739) was grown overnight at 37 °C in tryptic soy broth (TSB). TSB broth contains 17 g of pancreatic digest of casein, 3 g of enzymatic/papaic digest of soybean meal, 5 g of sodium chloride, 2.5 g of dextrose, and 2.5 g of potassium phosphate in 1-L of reagent-grade water [23]. To separate *E. coli* from the growth medium, the broth was centrifuged at 5000 rpm for 15 min and supernatant removed from the pellet. After washing the settled portion three times and removing supernatants, the bacteria was resuspended in distilled water, and then recentrifuged. The bacteria was finally washed and suspended in 10 mL distilled water, which was used as a stock solution for experiments made using the artificial wastewater. Appropriate dilutions of treated and untreated real wastewaters, which already include *E. coli* and TC were directly subjected to chlorine dioxide disinfection.

2.3. Chlorine dioxide generation

Liquid disinfectant solutions were prepared using a chlorine dioxide generator (ALLDOS, Oxiperm D164-005). The generator mixes $NaClO_2$ (7.5%, w/w) and HCl (9%, w/w) solutions in a small batch reactor where ClO_2 is produced in a gaseous form according to the stoichiometry given by the following equation [24]:

$$5NaClO_2 + 4HCl \Leftrightarrow 4ClO_2\,(g) + 5NaCl + 2H_2O \quad (1)$$

The gaseous is then contacted with by-pass water to dissolve ClO_2. Liquid chlorine dioxide was collected in dark glass bottles, which were sealed and stored at 4 °C. ClO_2 solution was prepared daily and its concentration was determined by DPD (the N,N-diethyl-p-phenylenediamine) method using a DR/2800 spectrophotometer (HACH, Co., USA). Chlorine dioxide concentration applied in disinfection experiments was ranged from 1 to 3 mg/L.

2.4. Disinfection experiments

All of the materials used in the experiments were autoclaved at 121 °C for 15 min. Disinfection tests were conducted at 20 °C. Initial concentration of *E. coli* in artificial wastewater samples was adjusted to 1×10^4–5×10^4/mL by injecting 0.1 mL of stock bacteria solution to the reactor. Similar bacteria densities were also observed in the real municipal wastewaters. A 200-mL COD-adjusted sample was placed in a 250-mL dark glass reactor. The pH of target wastewater samples was kept neutral using potassium buffer solution (PBS). The reactor was kept in a water-cooling bath to control the temperature of the disinfection samples around 20 ± 0.2 °C. After performing initial microbiological tests, various dilutions of treated and untreated wastewaters were disinfected with chlorine dioxide

Table 2
Physicochemical characteristics of the wastewaters.

Parameter	Unit	Artificial wastewater	Real wastewater	Secondary effluent
pH	–	6.8 ± 0.2	7.5 ± 0.1	7.7 ± 0.1
EC	μs/cm	95.9 ± 39.2	3184 ± 785	3638 ± 1097
Turbidity	NTU	5.3 ± 1.1	103 ± 95	14.22 ± 4.0
Alkalinity	mg/L $CaCO_3$	39.8 ± 3.7	1042 ± 180	862 ± 84
TSS	mg/L	<5	155 ± 92	21 ± 12.2
COD	mg/L	336.4 ± 18.5	240.8 ± 147.2	39.8 ± 17.4
BOD_5	mg/L	147.4 ± 22.6	139.8 ± 64.7	18.9 ± 14.8
NO_3-N	mg/L	2.84 ± 0.72	2.4 ± 1.7	0.98 ± 0.65
NH_4-N	mg/L	1.33 ± 0.5	23.7 ± 6.2	2.62 ± 2.1
PO_4-P	mg/L	6.9 ± 1.5	5.8 ± 3.8	2 ± 1.3

for 10 min. Each experiment was always repeated four times. Chlorine dioxide residuals were measured at different times through each disinfection experiment. It is important to note that dark colored pipette tips were used for the addition of the disinfectant, since ClO_2 decomposes quickly when exposed to light. In addition, radial forces cause the decomposition or stripping ClO_2 from liquid, so the wastewater samples were gently mixed on a magnetic stirrer through the disinfection process.

2.5. Microbiological analysis

The bactericidal efficiency of chlorine dioxide was assessed by comparing the number of microorganisms measured before and after the disinfection. Detection and enumeration of the bacteria were done by membrane filter procedure [22]. Before and after a disinfection process, 1–2 mL subsample was withdrawn from the reactor and diluted suitably so that the count on per petri would be between 20 and 100. To prevent the further disinfection effect of residual ClO_2, sodium thiosulfate (0.002 M) was initially added to the dilution waters. After metal vacuum filtering set was sanitized with gas flame, various volumes of the diluted subsamples were filtered directly from sterile 0.45 μm membrane filters (Sartorius 13906-50-AJN). For bacteria enumeration, filters were incubated for 22 ± 2 h at 37 °C on ENDO medium (Sartorius, ref. 14068-50-N). Once the incubation period was completed, all colonies for TC and dark red colonies with metal sheen for *E. coli* on ENDO medium were counted using an optic counter. Results were multiplied by dilution factors and the number of bacteria was always expressed as CFU/mL.

3. Results and discussion

3.1. Inactivation of microorganisms by chlorine dioxide

Figs. 1 and 2 show the inactivation of *E. coli* and TC, respectively during the disinfection of untreated artificial and real municipal wastewaters, and secondary effluent of various organic loads and disinfectant concentrations. Error bars in the figures represent two standard deviations of the mean log reductions from four replicate experiments. Using *t*-test, the inactivation data showed no statistically significant differences (at $\alpha = 0.05$) between the killing effect of chlorine dioxide on *E. coli* in artificial and real domestic wastewaters (Fig. 1). The experimental data also showed no statistically significant differences (at $\alpha = 0.05$) between *E. coli* and TC inactivation during the disinfection of the real domestic wastewater (Figs. 1 and 2). If large variations in the COD concentrations of the treated and untreated wastewaters are taken into account, it can be considered that the bacteria inactivation was slower in the secondary effluent. For example, *E. coli* and TC inactivations in the raw wastewater samples of 75 mg/L COD were significantly higher than those obtained in the secondary effluent with lower COD values of 12.5–50 mg/L. The exact reason for such decreased disinfection efficiency might be associated with greater resistance of older microorganisms or higher concentrations of reduced organic and inorganic species such as sulfide, ammonia, and phenolic compounds in the treated water [11,25]. This subject was clarified after examining chlorine dioxide residuals in the disinfected samples.

For all wastewaters the bactericidal effect of chlorine dioxide on *E. coli* and TC inactivation significantly decreased by increasing the water COD concentration. At 1 mg/L of ClO_2, the reduction in the number of bacteria was generally less than 1-log during the disinfection of untreated artificial or real domestic wastewater of different organic loads. Results from the disinfection assays conducted at 2 and 3 mg/L of ClO_2 indicated that the log inactivation of *E. coli* and TC in the untreated wastewater samples increased by two- to threefold when the COD concentrations were reduced by half. It should be noted that such analyses are valid for the range of COD and ClO_2 concentrations used in this study, so out of these ranges of disinfectant doses and organic loads, exact enhancement

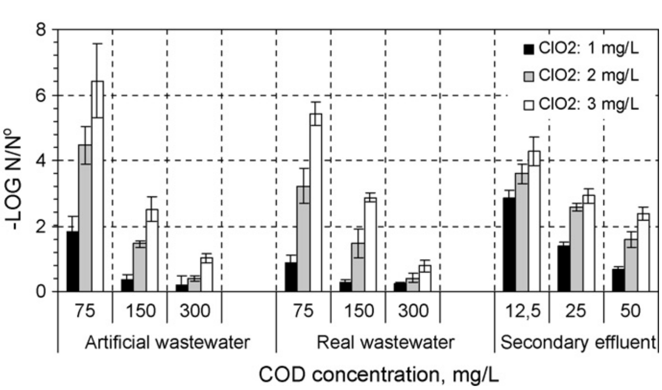

Fig. 1. Inactivation of *E. coli* for disinfection of various wastewaters by chlorine dioxide.

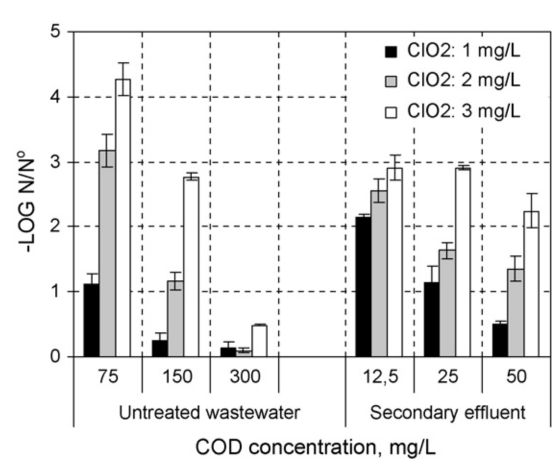

Fig. 2. Inactivation of TC for disinfection of various wastewaters.

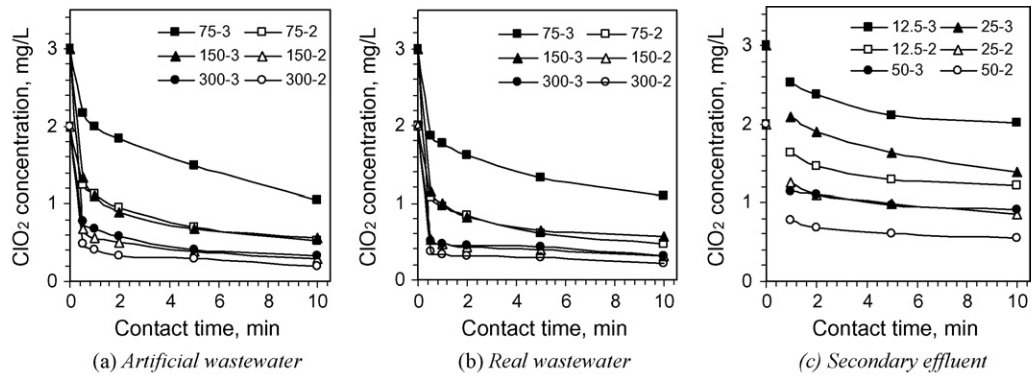

Fig. 3. Chlorine dioxide residuals during disinfection of treated and untreated wastewaters.

on the bacteria removal with respect to decreasing COD level might change. For the disinfection of the secondary effluent at 1 or 2 mg/L of ClO_2, log reductions in the number of *E. coli* and TC increased by a factor of 1.5–2 when the COD concentration decreased by 50%. But at 3 mg/L of disinfectant dose the improvement on the bacteria log inactivation with respect to decreasing organic load by half was lowered to a factor of 1.0–1.5. It appears that the effect of organic load on the bacteria killing was more obvious at lower disinfectant doses and higher water COD concentrations. These results are in agreement with those previously reported by Chang et al. [15] that have shown the unfavorable effect of dissolved organic carbon on the inactivation of *E. coli* by chlorine dioxide. They found that at 0.5 mg/L of the disinfectant doses the bacteria inactivation rate decreased approximately by a factor of 2 when the DOC concentration was doubled.

3.2. Analyses of residual disinfectant concentrations

To verify the unfavorable effect of the organic load on the bacteria inactivation, chlorine dioxide concentrations in target wastewaters were measured at appropriate time intervals through each disinfection process (Fig. 3). Chlorine dioxide residuals obtained at 1 mg/L-initial disinfectant dose were not included in the figures, since they were similar with smaller values shown on the graphs. Residual ClO_2 concentrations were expectedly higher in the samples of lower COD concentrations. Because chlorine dioxide quickly reacts with organic compounds, its concentration rapidly decreased in the first few minutes, and then slightly changed through the end of disinfection. As can be seen from Fig. 3, change on ClO_2 concentrations in artificial and real wastewaters followed similar trends explaining the comparable results attained for the inactivation of *E. coli* in these liquids.

Results from the analysis of chlorine dioxide residuals revealed that the decreased disinfection efficiency in the secondary effluent cannot be related to the reduced-species such as sulfide, ammonium, or other organic and inorganic compounds, since higher disinfectant residuals were found during its disinfection. It appears that the decreased *E. coli* and TC inactivation rates in the secondary effluent were most likely associated with the age of the microorganisms. Old bacteria are more difficult to kill than young bacteria, since they form polysaccharide shells over their cell walls, which support them more effectively against disinfectants [25]. The bacteria in the secondary effluent would grow older than those in the raw wastewater as the activated sludge treatment includes a sludge-recycling unit.

3.3. Correlation of bacteria inactivation

To examine the bactericidal effect of chlorine dioxide during wastewater disinfection, suitable kinetic models were fitted to the inactivation data. Chick and Watson model has been frequently used for the correlation of bacteria inactivations and applied also

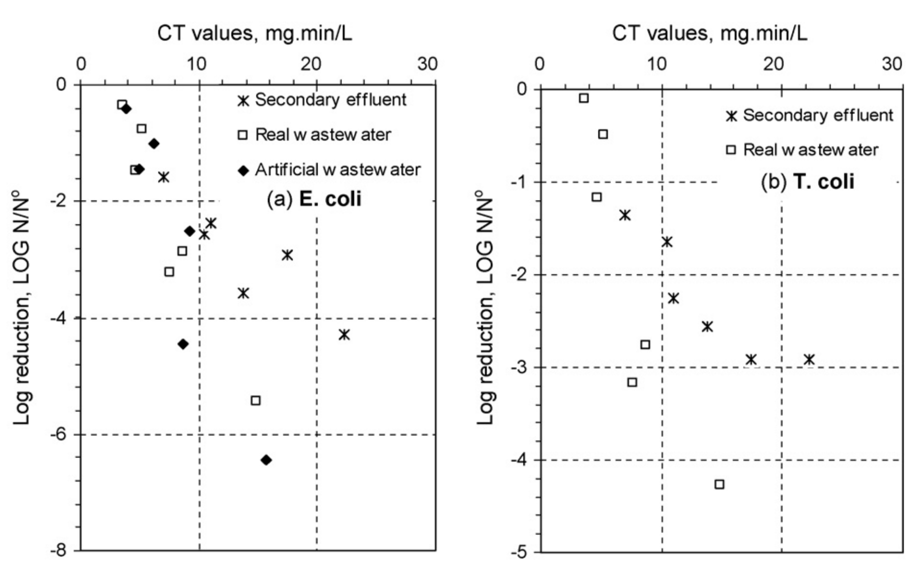

Fig. 4. Plot of inactivation data using *CT* values.

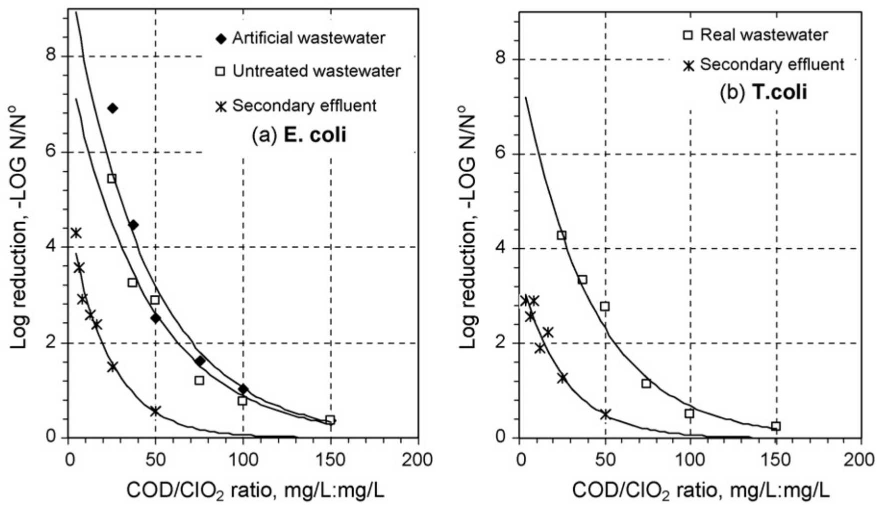

Fig. 5. Plot of inactivation data using COD to ClO_2 ratios.

to our experimental data:

$$\text{Log}\left(\frac{N}{N^0}\right) = -kCT \quad (2)$$

where N^0 is initial number of bacteria in liquid (CFU/mL), N is the remaining number of bacteria after 10 min disinfection (CFU/mL), k is the first order bacteria inactivation rate constant (time^{-1}), C is the effective disinfectant concentration (mg/L), and T is disinfection contact time (min). *CT* values were calculated in units of mg min/L by computing the area remaining under the curves given by Fig. 3. The computed *CT* values were plotted against the corresponding bacteria log inactivations (Fig. 4). The linear correlation coefficients (r) for the plots in Fig. 4 (*CT* vs. Log(N/N^0) were in a range of 0.90–0.96. *E. coli* and TC inactivation during the disinfection process increased with respect to an increase in the *CT* value. Results from the correlation of the inactivation data using the *CT* values confirmed the reduced disinfection efficiency in the secondary effluent. As shown in Fig. 4, the rates of *E. coli* log inactivation in the artificial and real wastewater samples look comparable, but those are clearly smaller for the secondary effluent.

The log reductions in the number of *E. coli* and TC for the disinfection of three wastewaters by chlorine dioxide were also plotted against corresponding initial COD to ClO_2 ratios (Fig. 5). The bacteria log inactivation decreased exponentially by the ratio of COD to ClO_2 with regression coefficients (r) greater than 0.98. According to these results, it appears that the inactivation data can be better correlated using the ratio of organic load to initial disinfectant concentration. Similar with the results using *CT* values, for a given COD to ClO_2 ratio the killing effect of chlorine dioxide in artificial and real domestic wastewater looks comparable, but it decreases in the secondary effluent. For example, at a ratio of 50 to 1, about 3-log *E. coli* or TC log reduction can be attained with the disinfection of the untreated wastewater, while it is only about 0.5-log for the disinfection of the secondary effluent.

In a chemical disinfection process, disinfectant dose and exposure time are important variables for the bacteria inactivation. The higher the disinfectant dose and exposure time, the greater is the rate of bacteria inactivation [26]. When compared to that in wastewater, a chemical disinfectant activate much longer in drinking water due to its low organic load. For drinking water disinfection, *CT* values provide good correlations for bacteria inactivation, while for the wastewater disinfection; it seems that initial contact of ClO_2 with the microorganisms controls the disinfection efficiency.

4. Conclusions

In this study, an unfavorable effect of organic load in terms of COD on the efficiency of chlorine dioxide has been demonstrated with both experimental results and appropriate kinetic models. Compared to the correlations using the *CT* values, the bacteria inactivation seemed to be better explained with the ratio of COD to ClO_2 concentrations for the disinfection of treated or untreated wastewater. The killing effect of chlorine dioxide on the coliform bacteria was lower in the secondary effluent when compared to that in the untreated municipal wastewater. The reduced disinfection efficiency was attributed to the greater resistance of aged microorganisms in the effluent water. Results from this study can be used as a reference in determining and applying chlorine dioxide doses for the disinfection of a target wastewater to meet both direct and indirect discharge water quality standards.

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