# APPLICATION OF ULTRAVIOLET (UV) TECHNOLOGY ON WATER DECHLORINATION: INFLUENCE OF UV FLUENCE DOSE AND UV TRANSMITTANCE ON CHLORINE REMOVAL EFFICIENCY

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**Abstract:** Water dechlorination is required to remove chlorine residual (free and combined chlorine) formed as byproducts of chlorination treatment. Ultraviolet (UV) dechlorination method has advantages compared to other dechlorination methods. This method uses a powerful photon energy generated by low pressure (LP) and medium pressure (MP) UV lamps to break chemical bond of the residual chlorine into reactive free radicals ($\bullet OH^-$) and ($\bullet Cl^-$). Studies are needed to evaluate its removal efficiency and the effect of treatment conditions on the efficiency before applying this method to practical applications. This study evaluates the effectiveness of medium pressure UV technology on UV dechlorination and investigates the influence of operation conditions (UV fluence and UV Transmittance) on chlorine removal efficiency. The impacts of both UV fluence and UV transmittance variations on chlorine removal efficiency were observed. Results of this study indicate that chlorine reduces upon exposure of UV radiation and chlorine removal efficiency increases with the increasing of UV fluence dose and UVT. The maximum UV fluence dose applied in this study (513 mJ/cm$^2$) results in less than 25% of total chlorine reduction.

***Keywords:*** *Chlorination, Dechlorination, Ultraviolet (UV), UV dose, UV Transmittance*

***Abstrak:*** *Deklorinasi pada pengolahan air dibutuhkan untuk menyisihkan sisa klorin (klorin bebas dan terikat) yang terbentuk sebagai hasil samping dari proses klorinasi. Metode deklorinasi menggunakan sinar ultraviolet (UV) memiliki beberapa kelebihan dibanding metode lainnya. Metode ini menggunakan energi foton yang dihasilkan oleh lampu ultraviolet bertekanan rendah dan bertekanan sedang untuk memutuskan ikatan kimia sisa klorin menjadi ion bebas radikal ($\bullet OH^-$) dan ($\bullet Cl^-$). Namun, sebelum menerapkan metode ini dibutuhkan studi tinjauan efisiensi penyisihan klorin yang dapat terjadi, serta studi kajian pengaruh kondisi pengolahan terhadap efisiensi penyisihan Oleh karena itu, penelitian ini bertujuan untuk mengevaluasi efektivitas teknologi ultraviolet bertekanan sedang pada pengolahan deklorinasi, serta menginvestigasi pengaruh kondisi operasi, yakni dosis ultraviolet dan daya transmisi ultraviolet terhadap efisiensi penyisihan. Pengaruh dosis ultraviolet dan daya transmisi ultraviolet terhadap efisiensi penyisihan klorin menjadi tinjauan dalam penelitian ini. Hasil penelitian menunjukkan bahwa sisa klorin berkurang setelah air terpajan radiasi sinar ultraviolet. Selain itu efisiensi penyisihan sisa klorin meningkat dengan bertambahnya dosis ultraviolet dan daya transmisi ultraviolet. Dosis ultraviolet maksimum yang digunakan pada penelitian ini adalah 513 mJ/cm$^2$. Dosis tersebut menghasilkan efisiensi penyisihan sisa klorin kurang dari 25%.*

***Kata Kunci:*** *Klorinasi, Deklorinasi, Ultraviolet, Dosis ultraviolet, Daya transmisi ultraviolet*

## INTRODUCTION

Despite the disadvantages of chlorine disinfection, *e.g.*, possibility of disinfect-tion by-products (DBPs) formation, it remains the most widely used method for the disinfection of water and wastewater in the United State (Howe, J. et al, 2012) and probably worldwide. In this method, chlo-rine is usually introduced to the water as chlorine gas ($Cl_2$), sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(OCl)_2$) or chloroamine ($NH_2OCl$). Dissolution of each of these chlorine agents hydrolyzes the chlorine to form hypochlorous acid, HOCl. Hypochlorous acid can further be hydrolyzed into hypochlorite ion, $OCl^-$. This reaction is strongly dependent on pH of the solution with equilibrium constant pKa = 7.5 (at 25°C). These species, HOCl and $OCl^-$ are commonly referred to as "free chlorine residual" (Howe, J. et al, 2012). In the presence of ammonia, hypo-chlorous acid and hypochlorite ion react with the ammonia to form monochlor-

amine, dichloramine, and trichloramine, which referred to as "combined chlorine residual". Chlorination that converts all ammonia to either trichloramine or nitrogen gas is known as "break point chlorination". After the break point, all ammonia has been converted and thus the addition of chlorine will form free chlorine residual.

Although chlorine is a powerful disinfection agent, clorine residual cannot be tolerated by several industrial processes due to contamination and unwanted chemical reactions. It could accelerate corrosion of vessels, valves and piping, and could also cause damages to delicate process equipments such as reverse osmosis (RO) membranes and deionization (DI) resin units, *e.g*. cation and anion exchanger.

In the case of drinking water, chlorine affects the taste and odor of drinks and liquids (Spellman, 2013). Recent studies suggest that chlorines (and other disinfectant agents) may react further with dissolved organic matter then form a range of DBPs such as the trihalomethanes (THMs), haloacetic acids (HAAs), and chlorite (Hebert et al, 2010). Some of these emerging DBPs may pose unintended health hazards. Until recently, health risks studies were directed primarily toward linking chronic DBPs exposure and cancer initiation or mutagenicity (Richardson et al, 2002). In the case of wastewaters effluent, research conducted by Watson et al (2012) concludes that DBPs formed in the chlorinated wastewaters can be toxic and may have a deleterious impact on aquatic organisms. Therefore, residual chlorine often must be removed once it has performed its disinfection function. The removal of residual chlorine is known as dechlorination.

Several technologies of dechlorination have been developed, including natural attenuation, chemical declorination, activated carbon, and ultraviolet (UV) technology. The latest technology, UV radiation, is generally produced by low pressure (LP) and medium pressure (MP) UV lamps that contain an inert gas, e.g. argon, and a small amount of liquid mercury (Linden & Sharpless, 2003). The LP lamps emit essentially monochromatic light at 254 nm wavelength, whilst the MP lamps radiate various outputs ranging from about 205 nm to above 500 nm wavelength (Linden & Sharpless, 2003).

When a potential energy is applied to the lamp, some of the liquid mercury vaporizes and collides with free electrons and ions, and thus increases the energy state of mercury vapor. The mercury with higher energy state tends to return to its normal energy state by discharging energy in the form of UV light (Clarke, 2006). This energy is then used to break down chemical bond of the residual chlorine. In the photodecomposition reactions of free chlorine in water, various primary reactive intermediates are formed which are rapidly converted into hydroxyl radical (•OH) and chlorine radical (•Cl) (Buxton & Subhani, 1972). Bolton (2010) and Feng et al. (2007) stated reactions occur in radiation of chlorines, such as:

$$HOCl + \text{UV photons} \rightarrow {}^{\bullet}OH + Cl^{\bullet} \quad (1)$$

$$OCl^{-} + \text{UV photons} \rightarrow {}^{\bullet}O^{-} + Cl^{\bullet} \quad (2)$$

$${}^{\bullet}O^{-} + H_2O \rightarrow {}^{\bullet}OH + OH^{-} \quad (3)$$

The advantages of UV dechlorina-tion compared to other technologies include:

1. No mixing or contact tanks are needed.
2. No chemical addition is required.
3. Minimum operation and maintenance required.

In addition, it leaves no impact on the taste, odor, color, and pH of water. However, there is a lack of information on UV dechlorination. The removal efficiency needs to be considered before applying this method. Thus, this study was undertaken to investigate the effectiveness of a medium pressure UV technology in water dechlorination and evaluate the influence of operation conditions (UV fluence and

UV Transmittance) on chlorine removal efficiency.

## MATERIAL AND METHODS

The experiments were carried out at CAWT (Centre for Advanced Water Technology) Laboratory in Singapore using a collimated beam UV apparatus (Atlantium Technologies, Ltd) equipped with a medium pressure (MP) UV lamp to generate polychromatic UV light. MP lamps operate at temperatures range of 600-900°C and at mercury vapor pressures of 2 – 200 psi (Clarke, 2006).

Each sample was placed in a 6-cm Petri dish and was exposed to the UV light over the specified exposure time. The water samples used for the experiments were the drinking water produced by Choa Chu Kang Water Works of Singapore. The raw water of this water treatment plant was extracted from Kranji Reservoir which would then be treated via coagulation, sedimentation and sand filtration, followed by chlorination as disinfection unit.

Chlorine concentrations were measured before and after the UV exposure over the duration of the experiments in order to calculate the chlorine removal efficiency. Each experiment was performed twice (duplicate). All experiments were conducted at ambient temperature (23 ± 2°C). Schematic of the collimated beam apparatus is illustrated in Figure 1.

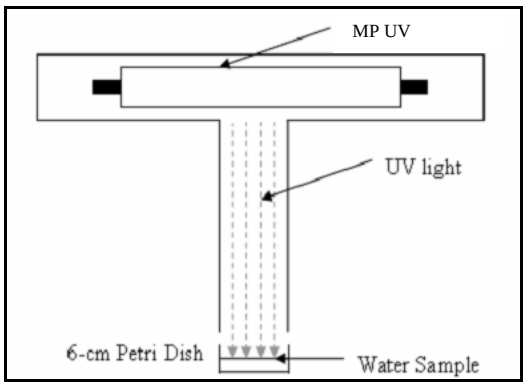


**Figure 1.** Schematic of the laboratory experiments set up

### Chlorine residual analysis

N,N-diethyl-p-phenylenediamine (DPD) colorimetric method is considered as the most widely used method for analyzing free and total chlorine in water and wastewater (Harp, 2002). The chemical basis for the DPD chlorine reaction is presented in Figure 2. In the experiments, concentration of total and free chlorine were analyzed by DPD colorimetric method using two types of reagents—DPD Free Chlorine Reagent and DPD Total Chlorine Reagent—for 10-ml of sample produced by Hach Permachem Reagent.

The DPD amine (reagent) was added to the water sample and was oxidized by chlorine contained in the sample to two oxidation products. The first compound was known as Würster dye that was relatively stable and creates the magenta color at neutral pH. The intensity of the color was then measured photo-metrically. The second compound, imines, was relatively unstable and colorless that would be formed at higher oxidant levels, *i.e.* higher chlorine concentration.

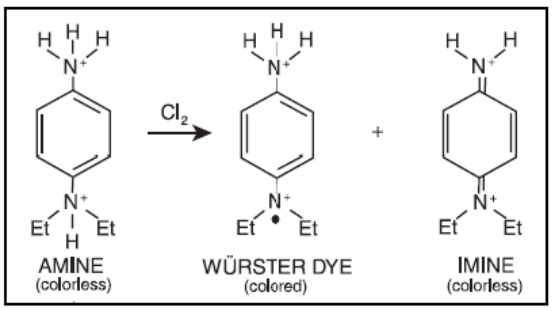


**Figure 2.** DPD-Chlorine Reaction Products *(Harp, 2002)*

### Variables of the Experiments

The control variable of the experiments was the total chlorine concentration which was 2 mg/L. Since chlorine is a highly oxidative compound, an equal chlorine concentration was difficult to achieve. Therefore, the concentrations were set of to be within the range of 1.90 mg/L to 2.2 mg/L. Two independent variables were designed: (1) UV fluence dose and (2) UV transmittance (UVT). The dependent variable was the decreasing amounts of

total and free chlorine concentration that represents the removal efficiency of UV dechlorination.

**UV Fluence Dose Variations**

Since UV fluence rate of the UV collimated beam apparatus in a laboratory scale is a fixed value, the UV fluence dose variations were achieved by varying the duration of time exposure of the sample under the UV light. The exposure time variations were 10, 20, and 30 minutes.

The fluence rates were measured by a radiometer Model SEL240 UV Curing Radiometer, Internal Light Inc, an instrument that is typically used in UV fluence rate measurements. It consists of a highly sensitive electronic ammeter connected to a UV sensor head, which generates a current proportional to the incident fluence rate. It can be used to measure UV fluence rate of a collimated beam apparatus by setting its radiometer detector head at the same height as the surface water in Petri dish. Results of the UV irradiance of the UV beam are presented in Figure 3.

In the experiments, 2 cm distance of the water surface and the UV apparatus was selected, which according to Figure 3 is equal to the UV fluence rate of 0.285 mW/cm$^2$. The UV fluence doses were calculated as the multiplication of UV fluence rate and the exposure time, which were 171, 342, and 513 mJ/cm$^2$.

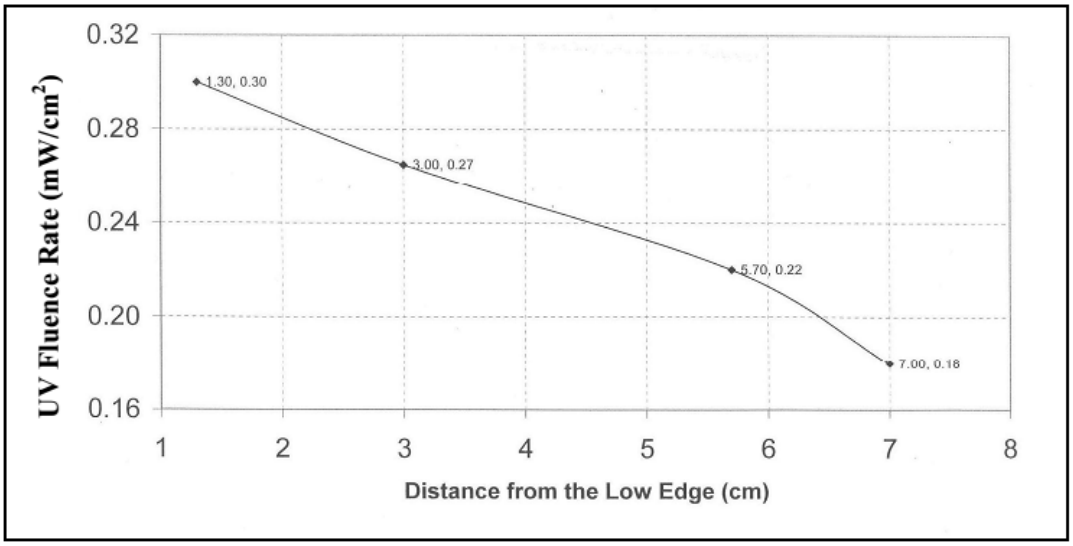


**Figure 3.** UV Fluence Rates of Collimated Beam Apparatus at Varied Exposure Distance

**UV Transmittance Variations**

The UVT concept is defined on basis of the Beers Law that is illustrated in Figure 4. UVT is the fraction of the emitted UV light that passes through the substance or in other word (*P*/*Po*), which is usually expressed in percent. The greater the amounts of particles that can absorb the UV light contained, the more of a reduction in UVT value. UVT is related to UV absorbance (UVA) according to the expressions written in Figure 5.

UV absorbance value depends on the quality of water sample. In the experiments, variations of UV absorbance were achieved by adding coffee stock solution (900 mg/L) into the samples. The coffee stock solution was made by addition of coffee powder into de-ionized (DI) water. An Agilent 8453 Diode Array Spectrophotometer (Global Medical Instrumentation, Inc) was used to determine the UV transmittance. The UV transmittance variations used in the experiments with their absorbance and transmittance value are presented in Table 1. The possibility of reactions between coffee and chorine were observed to

determine the interference that may occurred. For this purpose, the same amounts of chlorine were added to the sample A (no coffee), sample B (contains 9 mg/L of coffee), and to the sample C (contains 18 mg/L of coffee).

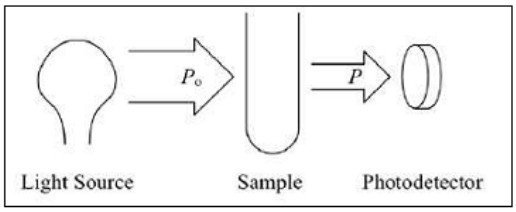


**Figure 4.** UV Transmittance Analogy

$$UVA = \log_{10}\left(\frac{100}{\%T}\right) = 2 - \log_{10}\%T$$

$$UVA = \log_{10} UVT = \log_{10}\left(P/Po\right)$$

$$UVT(\%) = 100T = 100P/Po$$

**Figure 5.** UV Transmittance and UV Absorbance expressions

**Table 1.** UV absorbance variations

| Sample | Coffee (mg/L) | UVT (%) | UV absorbance |
|---|---|---|---|
| Blank (DI water) | 0 | 100.00 | 0 |
| A | 0 | 93.279 | 0.03022 |
| B | 9 | 88.132 | 0.05487 |
| C | 18 | 83.566 | 0.07797 |

Each sample was kept in a dark place since light exposure would reduce chlorine contained in the samples. Chlorine concentration of each sample was then measured at different times to determine the decreasing concentrations of total and free chlorine.

## RESULT AND DISCUSSION

### UV Light Transmittance

Results from the coffee interference experiments, which are presented in Table 2 and Table 3, show that concentration of total and free chlorine in each sample (contains and not contain coffee) decreased in about an equal percentage. Thus, it can be concluded that there was no reaction occurred between chlorine and the components of the coffee. The amounts of chlorine depleted are considered as chlorine demand of the water sample, *i.e.* the amounts of chlorine that is required to oxidize impurities in the water (Tchobanoglous et al, 2003).

However, the results also suggest that coffee interferes with the DPD colorimetric measurements. This can be seen from the initial concentration of each sample (concentration at time = 0).

**Table 2.** Total Chlorine Concentration at Different Times (Coffee Interference Experiments 1)

| Sample | Total Chlorine Concentration (mg/L) at different times | | Chlorine removed (%) |
|---|---|---|---|
| | 0 min | 40 min | |
| A | 1.77 | 1.68 | 5.08 |
| B | 1.33 | 1.26 | 5.26 |
| C | 1.21 | 1.15 | 4.96 |
| Standard Deviation | 0.29 | 0.28 | 0.15 |

**Table 3.** Free Chlorine Concentration at Different Times (Coffee Interference Experiments 2)

| Sample | Total Chlorine Concentration (mg/L) at different times | | Chlorine removed (%) |
|---|---|---|---|
| | 0 min | 40 min | |
| A | 1.42 | 1.34 | 5.37 |
| B | 1.06 | 1.01 | 5.08 |
| C | 0.97 | 0.91 | 5.99 |
| Standard Deviation | 0.24 | 0.23 | 0.46 |

Initially, samples had the same chlorine concentration whilst the results show three different concentrations, *i.e.* the initial concentration of sample B and sample C were much less than that in sample A. This is likely to happen since coffee reduces the intensity of Würster dye color formed by the reagent and the chlorine and thereby decreases the readings of chlorine DPD colorimetric. Hence, calibration curves were made to determine the actual chlorine concentrations contained in sample B and sample C.

### Calibration Curves Determination

Data for calibration curves were obtained by adding the same amounts of chlorine

ranging from 0.2 mg/L to 2.15 mg/L into each sample followed by measuring its total and free chlorine concentration. The calibration curves were made for each sample—sample B and sample C—for total and free chlorine by making linear regressions over the data with concentrations measured in sample A (actual chlorine concentrations) as y-values and concentrations measured in sample B and sample C (concentration interfered by the coffee) as x-values. The calibration curves obtained are presented in Figure 4 and Figure 5.

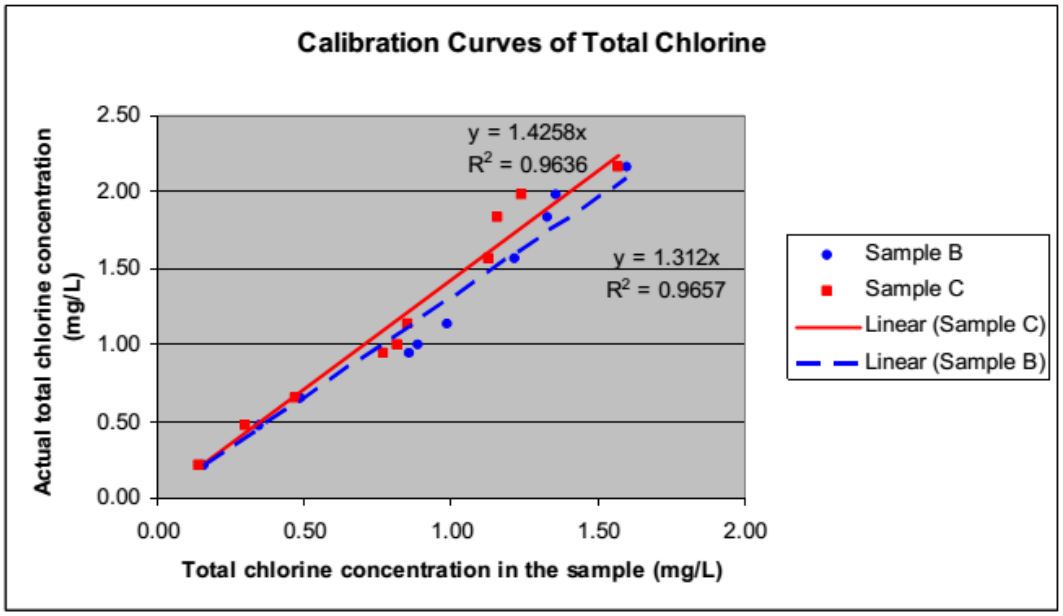


**Figure 4.** Total Chlorine Calibration Curves

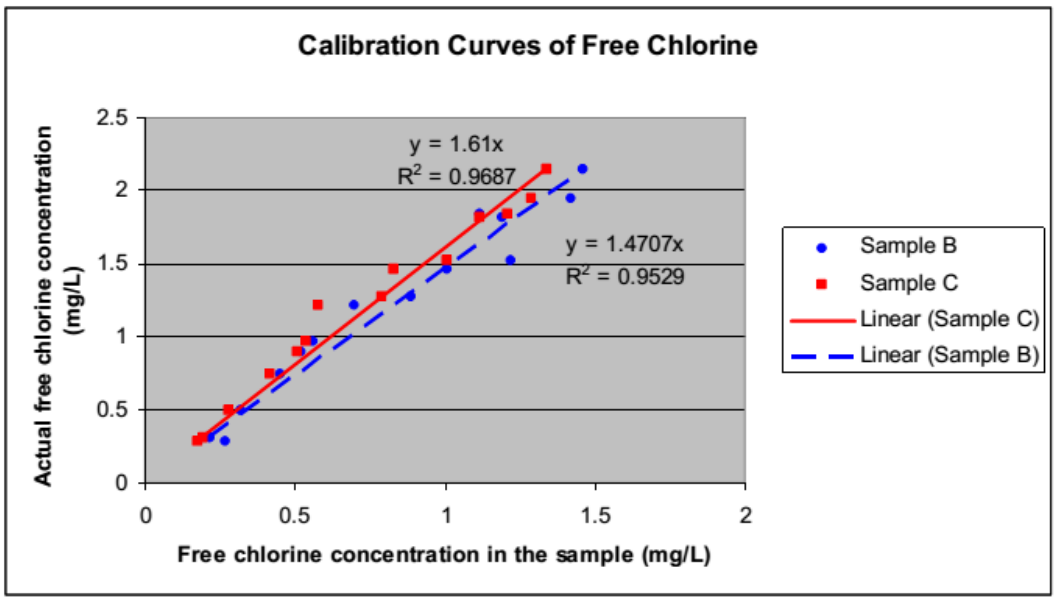


**Figure 5.** Free Chlorine Calibration Curves

**Influence of UV fluence dose to the chlorine removal efficiency**

Results of the chlorine removal efficiency illustrated in Figure 6 show that the total removal efficiency increases as the UV fluence dose increases. These results are consistent with other reported results (Örmeci et. al, 2005; Watts and Linden 2007). Thisresult is due to the fact that a higher UV fluence dose transfers greater amounts of energy to the solution, which was used to break the chemical bonds of free and combined chlorine.

In terms of chlorine removal efficiency, the results show that the range of UV fluence dose commonly applied for drinking water UV disinfection, 0-100 mJ/cm$^2$ (Watts and Linden, 2007), provides considerably low chlorine removal efficiency. In fact, the highest UV fluence dose (513 mJ/cm$^2$) applied in the experiments only resulted in less than 25% of chlorine removal efficiency. Further study is needed to investigate required fluence dose to achieve better removal efficiencies.

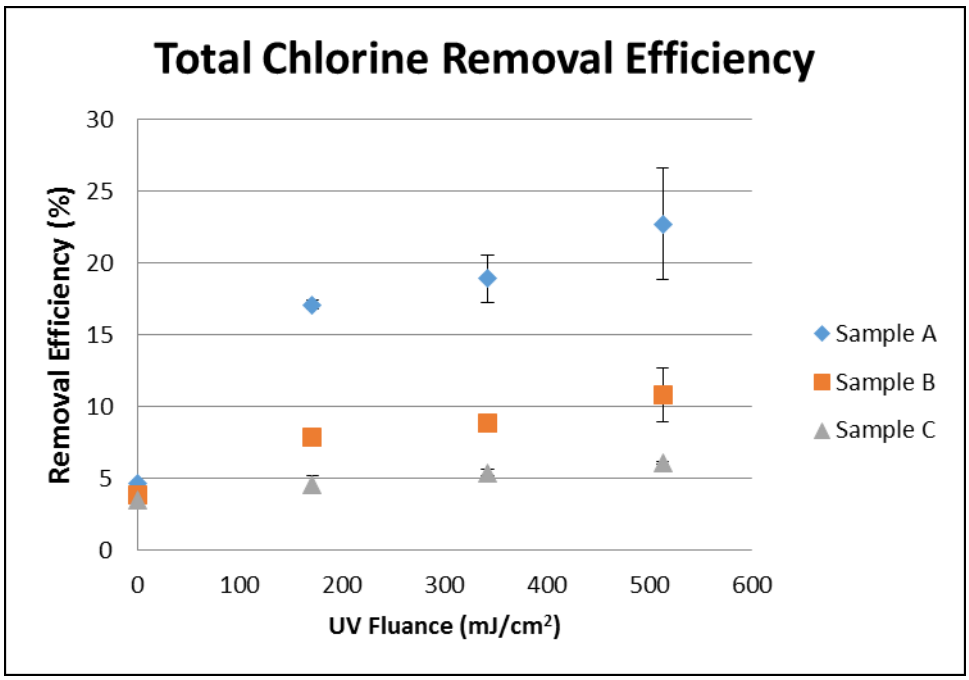


**Figure 6.** Total Chlorine Removal Efficiency

As shown in Figure 6, the total chlorine removal efficiencies are nonzero at UV Fluence 0 mJ/cm$^2$. This occurs likely due to the characteristics of chlorine which is highly oxidative. Hence, addition of chlorine will initially be utilized to oxidize the organic and inorganic com-pounds of water samples such as BOD, DOC, TOC, Nitrite, Nitrate, Iron, and Manganese (Tchobanoglous et. al., 2003). It can also be concluded that the removal efficiencies achieved in this study are inclusive of the chlorine demand of water samples. The organic and inorganic compounds of water samples exerting chlorine demand are shown in Table 4.

The fluence dose variations in this study were achieved by lengthening exposure time, which in full scale water treatment means additional requirement of contact tank. This is inconsistent with the idea of gaining benefit from of UV technology itself. Thus study with full scale UV system is needed to confirm whether desirable removal efficiencies could be achieved.

Table 4. Characteristics of Water Samples Concerning Chlorine

| Parameters | Unit | Value | Method |
|---|---|---|---|
| $BOD_5$ | mg/L | <2 | APHA 5210B |
| DOC | mg/L | 1.99 | EPA 415.1 |
| TOC | mg/L | 2.34 | EPA 415.1 |
| Nitrate (as $NO_3$) | mg/L | 0.48 | EPA 300 |
| Nitrite (as $NO_2$) | mg/L | <0.01 | EPA 300 |
| Iron | mg/L | <0.003 | EPA 6010B |
| Manganese | mg/L | <0.003 | EPA 6010B |

**UVT influence to the chlorine removal efficiency**

Results of chlorine removal efficiency of each sample at different UV fluence dose and UVT in Figure 6 indicate that the total removal efficiency significantly decreases with lower UV transmittance value. This likely occurs since the UV light transmitted in the samples that contain coffee is absorbed by the coffee instead of used by the chlorine to break its chemical bonds. Since the UVT depends on the quality of water being treated, it can be concluded that water with poor quality has a lower UVT, and thereby results in a lower efficiency of UV Dechlorination. Thus, in the application of UV dechorination, pretreatments must be performed to improve the water quality in order to obtain higher chlorine removal efficiency.

## CONCLUSION

In this study, the effectiveness of a medium pressure UV technology in water dechlorination and the influence of operation conditions (UV fluence and UV Transmittance) on chlorine removal efficiency were investigated. The results proved that the UV light exposure reduces chlorine concentration in water samples. The results also suggested that UV fluence and UVT influence chlorine removal efficiencies. The total chlorine removal efficiency increases with the increasing UV fluence dose. The highest UV fluence (513 $mJ/cm^2$) applied in the experiments resulted in less than 25% of chlorine removal. However, removal efficiency significantly decreases as the UV transmittance value decreases. Water with poor quality has a lower UVT, and thereby resulting in lower removal efficiency. The results also indicate that the presence of coffee, or other substances that absorb light, interferes with the DPD colorimetric measurements. Hence, in the application of UV dechorination, pretreatments must be performed to improve the water quality in order to obtain higher chlorine removal efficiency.

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