Effect of Trichloroisocyanuric Acid Disinfectant Filled in Swimming Pool Water

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Abstract: This research was to study the appropriate conditions for using trichloroisocyanuric acid (TCCA) as disinfectant for swimming pools. The amount of TCCA required to release 1.0-3.0 mg/L of free residual chlorine (standard for the swimming pools) was 3.00 and 15.00 mg/L for the tap water and the synthetic swimming pool water, respectively. The addition of TCCA was controlled by oxidation-reduction potentiometer at 710-750 mV. The residual chlorine of 1.5 mg/L released from TCCA killed 100% of *E. Coli* and Fecal coliforms. The effects of time, temperature and various parameters such as pH, residual chlorine, combined chlorine, hardness, sulphate, alkalinity and cyanuric acid (CA) on concentration of TCCA application were studied. The results showed that the alkalinity was increased while the residual chlorine decreased with time. Temperature had no effect on every parameter. Studies of TCCA effectiveness used in swimming pools in Thailand, found that pH value was as low as 3.0. At this low pH level, teeth corrosion of swimmers was found, therefore TCCA usage needed to be controlled for maintaining the pH level. Sodium bicarbonate, sodium carbonate or sodium hydroxide should used to bring the pH up to 7.2-7.5 In case of high cyanuric acid (CA) concentration; HOCl concentration will be decreased, resulted in the ineffectiveness of disinfection due to the HOCl lock phenomenon. Therefore after pH adjustment, the sodium hypochlorite solution should be used instead of TCCA until CA concentration complied with the standard.

Keywords: Trichloroisocyanuric Acid, Cyanuric Acid, Chlorine, Swimming Pool, pH.

1. INTRODUCTION

At present, trichloroisocyanuric acid (TCCA) has been used increasingly in swimming pool waters across Thailand. Upon application to pool waters it can release disinfectant chlorine and cyanuric acid, acting as chlorine reservoirs [1-3]. Cyanuric acid can react with free chlorine in the pool waters to form N-chloro species [5]. These N-chloro species continuously hydrolyze to hypochlorous acid (HOCl) to form chlorine reservoirs that are not subject to photodegradation. Therefore, cyanuric acid is able to maintain chlorine residuals more easily and economically. However, the disadvantage of using TCCA was observed due to low pH of pool waters and high concentration of cyanuric acid affecting on people swimming in the pool. The standard national swimming pool recommends levels of the CA stabilizer in the 30-80 mg/L concentration range and pH level of pool waters in the 7.2-7.5 range [6].

The reason of low pH of pool waters when TCCA was used is that TCCA occur hydroxylation obtaining HOCl and cyanuric acid [7]. Then HOCl in water can hydrolyze to hydronium ion and hypochlorite which will decompose to chloride ion. Cyanuric acid also decomposes to hydronium ion and cyanurate. Higher concentration of hydronium in water, lower pH level of pool water could be observed. Higher concentration of CA provides disadvantage in chlorine protection. Beyond 30 ppm (mg/L) cyanuric acid becomes a deterrent rather that a help for allowing chlorine to do its job of killing bacteria and algae. It lessens chlorine's effectiveness because the chlorine becomes progressively over-stabilized. This leads to a situation known as "Chlorine lock". Chorine is "locked up" by the high levels of cyanuric acid [8], and is unable to work normally. Therefore, some pool operators misunderstood and added more TCCA in order to obtain higher chlorine's efficiency. It results in too much cyanuric acid built up in the water, causing in low pH of water. At high level of CA, there is also a carcinogenic hazard that needs to be avoided.

The present work provides the quantity of TCCA added in the swimming pool waters, following the standard national swimming pool, and including manages the problems that come with too much cyanuric acid and low pH of water. This is the first time that using TCCA as disinfectant in swimming pool waters has been studied in order to proper usage of TCCA for pool operators in Thailand and elsewhere.

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2. EXPERIMENTAL SECTION

Reagent

Cyanuric acid (90% Cl_2) commercial grade was purchased from Aldrich Chemical, Thailand. Sodium hydroxide, sodium carbonate and sodium bicarbonate were purchased from CARLO.

Sample

1. Tab water
2. Synthetic water was prepared from tab water and adjusted conditionally as same as pool waters by adding some chemicals that are found in body fluid. Using a body fluid analogue (BFA) in swimming pool waters opening for 12 hours, some chemicals in urine and sweat are shown in Table 1.

Table 1 some chemicals in urine and sweat 200 and 50 mL, respectively [9]

Constituent	Concentration (mg/L)	Carbon (mg/L)	Nitrogen (mg/L)
Ammonium Chloride	2,000	-	520
Urea	14,800	2960	6900
NaH_2PO_4	4,300	-	-
Citric acid	640	240	-

3. METODOLOGY

Relationship between the concentration of trichloroisocyanuric acid and various parameters

Tab water and synthetic water which had TCCA in the concentration of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 mg/L were measured for free available chlorine, total chlorine, sulphate, chloride, calcium hardness, cyanuric acid, alkalinity and pH. Free available and total chlorine were tested by DPD spectrophotometry at wavelength 515 nm [10]. For sulphate analysis, turbidimetric method was chosen and measured by spectrophotometer at 420 nm [10]. Chloride in water samples was measured by titration with silver nitrate. Calcium hardness was tested by titration with EDTA [10]. Alkalinity was determined by titration with sulphuric acid. Determination of cyanuric acid in water samples was measured by High Performance Liquid Chromatography (HPLC) [11]. pH meter was used for testing pH of water samples.

Relationship between various parameters and time

TCCA was added in tab water and synthetic water in order to obtaining the concentration of free chlorine in the range of 1.0 – 3.0 mg/L. Then water samples were collected at 0, 3, 6, 12, 24, 48 and 72 hours for measuring of pH and the concentration of free chlorine, monochloramine, dichloramine, trichloramine, sulphate, chloride, calcium hardness and cyanuric acid.

Relationship between various parameters and temperature

TCCA was added in tab water and synthetic water in order to obtaining the concentration of free chlorine in the range of 1.0 – 3.0 mg/L. Temperature of water samples was controlled at 20, 30 and 40 °C, respectively for a hour and then collecting for measuring of pH and the concentration of free chlorine, monochloramine, dichloramine, trichloramine, sulphate, chloride, calcium hardness and cyanuric acid.

Relationship between the concentration of trichloroisocyanuric acid and oxidation-reduction potential (ORP)

Tab water and synthetic water which had TCCA in the concentration of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 mg/L were measured for potential by oxidation-reduction potentiometer.

Adjusting low pH of water samples

TCCA was added in synthetic water in order to obtaining the concentration of 1,000 mg/L and the pH of 3. The solution was divided into 3 portions for adding gradually 100 mg/L of NaOH, Na_2CO_3 and $NaHCO_3$, respectively and recording total volume of base adjusting pH up to pH7.

Study of trichloroisocyanuric acid as disinfectant for killing E. *Coli* and Fecal coliforms

E. *Coli* were prepared for a number of 10^6 cell/mL in tab water (500 mL) adjusted pH to 7.2. Then water sample was added with 0.50 mg/L of TCCA. It was collected at 5, 10, 15 and 30 minutes for determining of E. *Coli* and residual free chlorine. E. *Coli* were changed to enterobacter and the experiment was repeated again. Next experiment was to mix E. *Coli* and enterobacter and repeat the procedure. The effect of concentration of TCCA was studied by changing the concentration to 1.50 and 3.00 mg/L, respectively.

4. RESULTS AND DISCUSSIONS

Relationship between the concentration of trichloroisocyanuric acid and various parameters

As in Figure 1, when the concentration of TCCA was increased, free chlorine in both tab water and synthetic water were also increased.

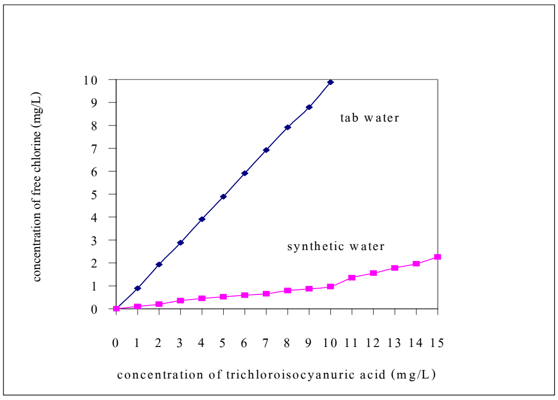

Fig. 1 Relationship between free chlorine and concentration of TCCA in tab water.

In tab water, it seemed that free chlorine obtained almost from hydrolysis of TCCA. For example, 2.00 mg/L of TCCA added in tab water would give 1.89 mg/L of free chlorine while in synthetic water; it required 11.00 mg/L of TCCA obtaining the same amount of free chlorine. Because of ammonia-nitrogen in synthetic water, free chlorine could combine with ammonia-nitrogen to give 3 types of compounds such as monochloramine, dichloramine and trichloramine. Figure 2 shows that chloramines have lower effect and cause more irritating than free chlorine.

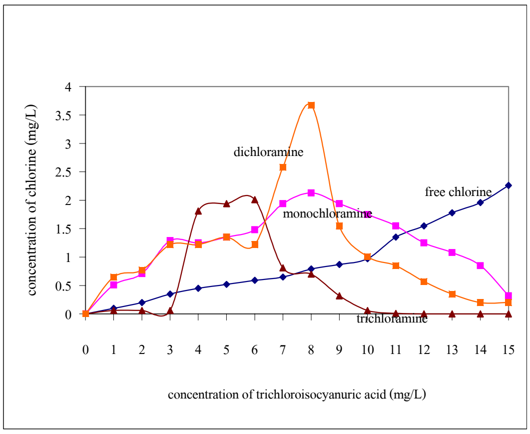

Fig. 2 Types of chlorine relating to concentration of TCCA (mg/L).

The standard national swimming pool recommends chloramines less than 1 mg/L, especially for monochloramine. Chloramines could be removed by adding free chlorine to ammonia in the ratio of 2:1 and then transformed to nitrogen dioxide as shown in eq. 1. Therefore, it required to add TCCA up to 15 mg/L for synthetic water.

$$NHCl_2 + NHCl_2 + HOCl \longrightarrow N_2O + 4HCl \quad (1)$$

Figure 3 and 4 represent that increased in TCCA in both synthetic water and tap water from 1.0 to 10.0 mg/L lead to decrease in alkalinity from 95 to 77 mg/L as $CaCO_3$ in tab water. It did not much affect on synthetic water that would slightly decrease from 72 to 68 mg/L as $CaCO_3$. Other parameters did not change when TCCA increased in both synthetic water and tap water.

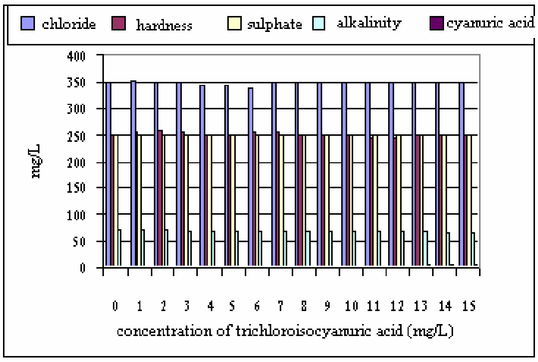

Fig. 3 changing in various parameters relating to concentration of TCCA (mg/L).

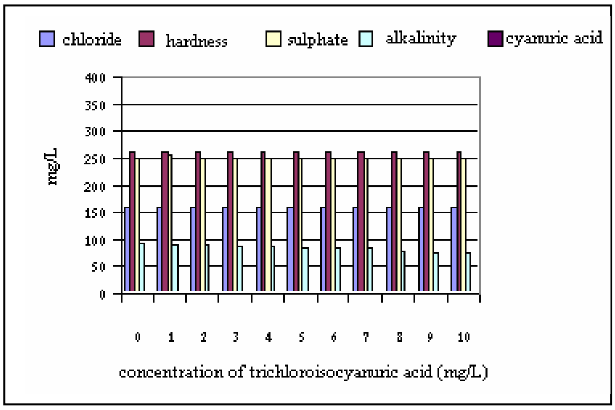

Fig. 4 changing in various parameters in synthetic water relating to concentration of TCCA (mg/L).

TCCA hydrolyses to hydronium ion and cyanuric acid which is weak acid. Although both hydrolysis products could decrease in alkalinity, it depends on water condition. In tab water, buffer condition resisted in changing alkalinity, therefore, it decreased slightly when TCCA increased.

Relationship between various parameters and time

As in Figure 5, concentration of free chlorine was decreased when time increased. Graph shows zero-order characteristic.

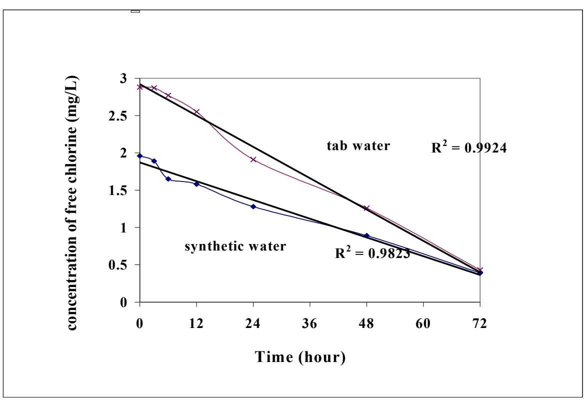

Fig. 5 Effect of time on concentration of fee chlorine in water samples.

From experiment, constant decomposition rate of free chlorine at each concentration and the suitable time for adding chlorine were obtained. Graph shows that constant rate is 0.042 from average value of each slope, calculating from eq. 2

$$C_t = C_0 - 0.042t \qquad (2)$$

C_t = concentration of free chlorine at any time
C_0 = initial concentration of free chlorine
t = time (hour)

As in Figure 6, it could explain about increasing in pH by following Henry's pressure law that carbon dioxide escapes from water when there is more carbon dioxide than air. When carbon dioxide escapes, equilibrium in eq. 3 will loss. Reaction proceeds in left direction, corresponding to decrease in hydrogen ion and increase in pH value up to 8.3. With this reason, pH of water could increase with time and no need to adjust pH with any chemicals.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow H^+ + CO_3^- \qquad (3)$$

As shown in Figure 7 and 8, chloride and alkalinity were slightly increased due to decomposition of free chlorine when time increased. Other parameters were not affected with time.

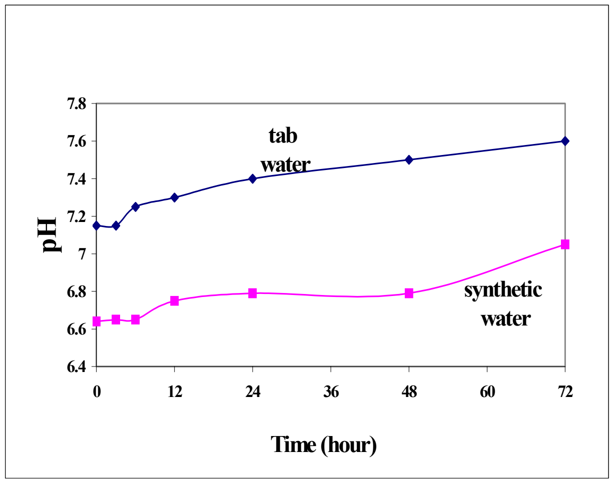

Fig. 7 Effect of time on various parameters of tab water.

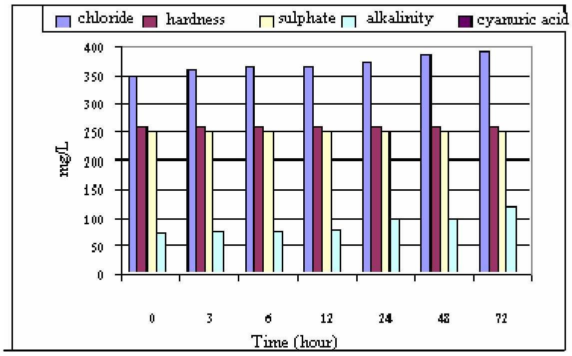

Fig. 8 Effect of time on various parameters of synthetic water.

Relationship between various parameters and temperature

The experiment was set in the purpose of studying in the suitable quantity of TCCA for any season. The results were shown in Figure 9 and 10 that changing in temperature did not affect on the concentration of free chlorine and other parameters. Therefore, TCCA could be added in pool waters at any season.

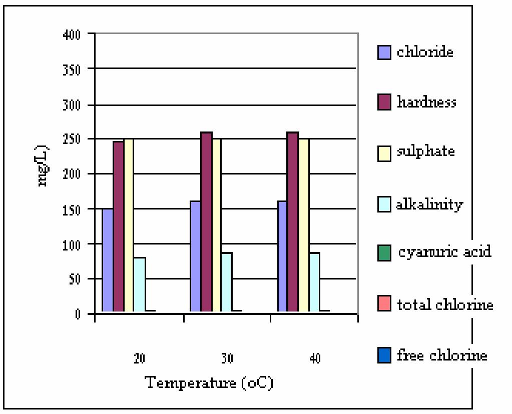

Fig. 9 Effect of temperature on various parameters of tab water

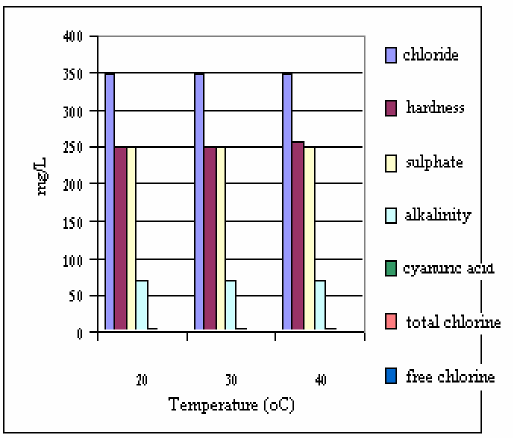

Fig. 10 Effect of temperature on various parameters of synthetic water

Relationship between the concentration of trichloroisocyanuric acid and oxidation-reduction potential (ORP)

Application of using oxidation –reduction potentiometer for controlling of free chlorine quantity in pool water was examined by studying in relationship with TCCA and free chlorine. From figure 11, it was found that 15 mg/L of TCCA corresponded with 710-760 mv, which was related to 1-3 mg/L of free chlorine as in Figure 12.

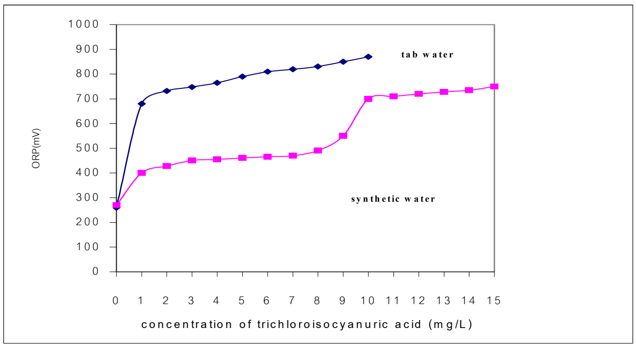

Fig. 11 Effect of TCCA on potential.

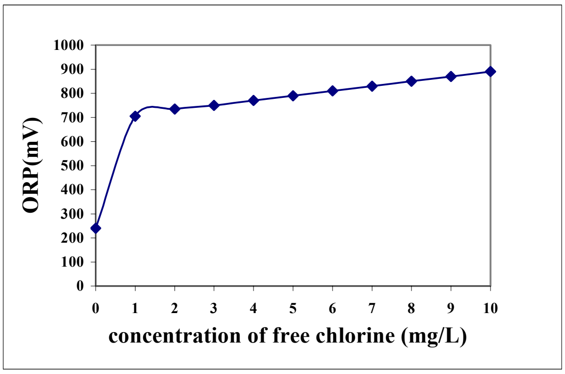

Fig. 12 Effect of free chlorine on potential.

In conclusion, when oxidation –reduction potential device is used for controlling of free chlorine in pool water, it should be set in the range of 710-760 mV in order to obtaining 1-3 mg/L of free chlorine that is the standard national swimming pool levels.

Adjusting low pH of water samples

In Thailand, pool operators do not control pH when TCCA has been added as disinfectant. In consequence, low pH of pool water has been founded and caused teeth corrosion in swimmer. This research studied the suitable base using for adjusting pH of pool waters. 500 mL of water samples adjusted pH of 2 was added with 100 mg/L of sodium hydroxide, sodium carbonate or sodium bicarbonate up to standard pH level. Graph was plotted for calculating the suitable amount of base adding in the pool (as eq. 4), and then taking water samples after adjusting pH for measuring various parameters.

$$\text{Amount of base (Kg)} = \frac{(B-A)\text{ mL} \times V\text{ m}^3}{500\text{ mL}} \times \frac{100\text{ mg/L} \times \text{L}}{10^3\text{ mL}} \times \frac{10^6\text{ mL} \times \text{Kg}}{\text{m}^3\ 10^6\text{ mg}}$$

$$= (B-A) \times V \times 2 \times 10^{-4} \quad (4)$$

V = volume of pool waters (m^3)
A = Volume of base at initial pH of pool water (mL)
B = Volume of base at required pH of pool water (mL)

As in Figure 13, sodium hydroxide was used the least amount of all bases for adjusting pH up to 7.2 – 7.5. Although sodium hydroxide was very strong base, it should be considered the cost of using all three bases.

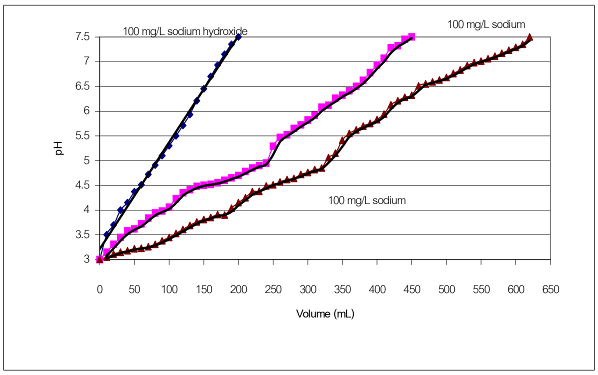

Fig. 13 volume of bases for adjusting pH of water samples.

Figure 14 shows various parameters before and after using sodium hydroxide, sodium bicarbonate and sodium carbonate.

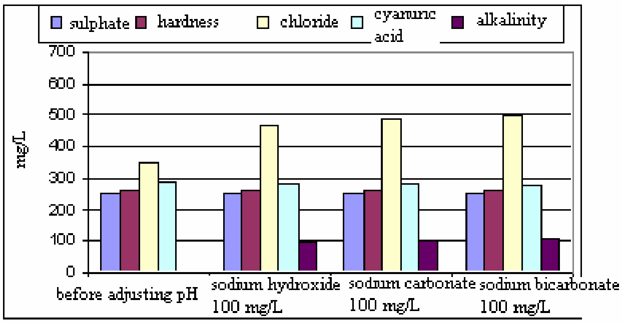

Fig. 14 Quality of water samples before and after adjusting pH.

Concentration of sulphate and calcium hardness did not change but alkalinity increased with pH. For chloride, it was increased from 350 mg/L to 490 mg/L because OH^- reacted with hydrochloric acid as in eq. 5

$$HCl + NaOH \longrightarrow H_2O + NaCl \quad (5)$$

Although sodium carbonate and sodium bicarbonate were used in larger amount than sodium hydroxide, the advantage of using sodium bicarbonate was to create buffer property and resist changing in pH as in Eq. 6.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow HCO_3^- \longleftrightarrow H^+ + CO_3^- \quad (6)$$

Study of trichloroisocyanuric acid as disinfectant for killing E. *Coli* and Fecal coliforms

From standard plate count method [12], it was found that 0.5 mg/L of free chlorine killed 100% of both E. *Coli* and enterobacter for 5 minutes. 100% of both bacteria would be killed at once when 1.5 mg/L of free chlorine was used.

5. CONCLUSION

The amount of TCCA required to release 1.0-3.0 mg/L of free residual chlorine (standard for the swimming pools) was 15.00 mg/L for swimming pool waters. Oxidation-reduction potential device was set in the range of 710-176 mv for controlling the amount of TCCA adding in pool waters. After adding TCCA, decreased in free chlorine, increased in pH and alkalinity and stability in sulphate, chloride and hardness were examined as time passed. Temperature did not have any effect on parameters; therefore, TCCA would be added any season. The suitable concentration of free chlorine for killing 100% of E. *Coli* and enterobacter at once was 1.5 mg/L. This concentration of free chlorine is in the range of the standard national swimming pool levels.

More TCCA, lower pH level in pool waters was measured. At this low pH level, teeth corrosion of swimmers was found, therefore TCCA usage needed to be controlled for maintaining the pH level. Not only low pH level was found in pool waters, but also high level of cyanuric acid that is hydrolyzed from TCCA was built up. This leads to a situation known as "Chlorine lock". Chorine is "locked up" by the high levels of cyanuric acid, and is unable to work normally. Therefore, some pool operators misunderstood and added more TCCA in order to obtain higher chlorine's efficiency. Therefore, adding TCCA requires being controlled the quantity in pool waters. Using sodium hydroxide can adjust pH up to standard level. Adjusting pH of pool waters improves the quality of water, decreases in teeth corrosion of swimmers, and increases in chloride.

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