Evaluation of disinfection efficiency between sodium hypochlorite and chlorine dioxide on spa water

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ABSTRACT

Recent government inspections have revealed high microorganism indices in spa water throughout Taiwan. Using spas has become a popular leisure activity because of its recognized health benefits. However, spa water at vacation resorts is often used by numerous visitors. This study compares microbial disinfection effectiveness between chlorine dioxide and conventional chlorine in spa water containing Chinese herbal medicine. Due to the complexity of the compounds in the pool and difficulty in measuring disinfection effectiveness accurately, this study was performed in a laboratory with actual spa water containing Chinese herbal medicine using either chlorine dioxide or sodium hypochlorite. Degradation is then compared by measuring residual chlorine dioxide concentrations and safe disinfection doses in the simulated solution. Regarding total colony forming unit level, the equivalent concentration required for spa water to meet government standards is 0.7 mg L^{-1} as ClO_2 or 1.8 mg L^{-1} as Cl_2. Disinfection efficiencies are 99.4 and 89.5% for chlorine dioxide and sodium hypochlorite, respectively. Generally, chlorine dioxide is more effective than sodium hypochlorite and is clearly safe. The data in this study can improve the disinfection technology used by related businesses to enhance water quality.

INTRODUCTION

Strong economic growth has dramatically increased living standards in Taiwan. Gymnastics buildings and health clubs combining herbal spas, amusement parks, and body building facilities are now common throughout the country. Specifically, herbal spas are usually quite crowded and heavily used. When many people swim and bathe in herbal spas, sweat and other substances can make the pools dirty, and microorganisms can grow rapidly if the pools are improperly managed. Therefore, the sanitization and disinfection of herbal spas must be regulated to provide a clean environment for public use. Research in sterilization and disinfection of spa water is essential for ensuring water quality and safety. In Taiwan, each city and county sets up its own water quality standards for herbal spas. The general requirements for free residual chlorine concentrations in pool water range between 1.0 and 3.0 mg L^{-1}. To comply with these rules, spas are often chlorinated with bleach power, bleach liquid, or sodium hypochlorite until the free chlorine concentrations reach 1.0-3.0 mg L^{-1}. Free chlorine levels must be adequately controlled. Excessively high levels can produce irritating odors in both the water and the air near the spas and can also cause symptoms such as headaches and nausea [1]. Pool water is often chlorinated when excessive microorganisms are detected. Chlorination is a simple and economic disinfection method. Since the mid 1970s, chlorination has played an important role in decreasing the incidence of typhoid fever, controlling infectious intestinal disease, and increasing the effectiveness of water purification. However, chlorination causes formation of byproducts resulting in unhealthy halogenated hydrocarbons. Potable water tests in the U.S.A. show that halogenated hydrocarbon substances exist universally [2,3]. For example, carcinogenic disinfection by-products (DBPs) are known to accumulate after chlorination. Trihalomethanes and haloacetic acids are thought to be the most important of these DBPs [4]. Sometimes, pool water is treated with heat, but this may be ineffective if thermophiles are present in spa water.

Chlorine dioxide is recognized internationally as the best chlorine disinfectant. Chlorine dioxide has good absorption and penetration qualities and can effectively oxidize sulfur-based enzymes [5]. The conversion rate of chlorine dioxide is as high as 90%, so the recession mechanism of chlorine dioxide is elec-

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tron formation by chlorite ions. Therefore, what could be interpreted as chlorine dioxide disinfection may not actually produce chlorinated organic compounds. Since chlorine dioxide is a reactive compound, it quickly decomposes in the natural environment. In water, chlorine dioxide is formed using ClO_2^-; chlorine dioxide and chlorite are not present in the food chain. Chlorite and chlorate salt concentrations are also minimal and are not components of other derivatives. It also rapidly controls the synthesis of microbial protein so as to destroy microorganisms to achieve sterilization and disinfection [6]. Therefore, its application in disinfection and sterilization in urban sewage sterilization and disinfection has been studied intensively.

Spas in vacation resorts are often used by numerous visitors. This study compared chlorine dioxide application with conventional chlorine in terms of their microbial disinfection effectiveness in a spa pool containing Chinese herbal medicine. Due to the complexity of the compounds in the pool and the difficulty measuring the disinfection effect, spa water containing Chinese herbal medicine was used in laboratory. The spa water is then used to study bacterial degradation, residual chlorine dioxide concentration, and optimal disinfection dose. These studies were expected to obtain the disinfection technology needed by related businesses to improve their water quality control capability.

MATERIALS AND METHODS

1. General Description

This study analyzed a modern indoor herbal spa club located in Tainan County, Taiwan. Water sample gathering, handling, data extraction, and data analysis were performed according to NIEA Guidelines issued by the Taiwan Environmental Protection Agency [7].

2. Procedure

Disinfection experiments were simulated in the laboratory. Water samples from a local spa were collected and analyzed for bacterial levels. The microorganisms in the water samples were cultivated. Finally, various ClO_2 and sodium hypochlorite concentrations were applied to the water samples.

(1) Procedure for Spa Water Sampling for Chemical Analysis:
   a. Sanitize sampling bottles with nitric acid (1 + 9 nitric acid solution) or hydrochloric acid (1 + 5 hydrochloric acid solution) and rinse with clean water.
   b. Fill bottles with spa water obtained from three areas of the spa: maximum, medium, and minimum depth. The water was collected 30 cm below the surface and 1 m from the edge of the spa without leaving air pockets in bottles to prevent oxygen from getting into samples.
   c. For each sample, measure pH, temperature, conductivity, free chlorine level, ammonia, nitrate, and nitrite.

(2) Spa Water Sampling for Bacterial Analysis:
   a. Use sterile sampling bags to obtain spa water samples to avoid contamination during sampling.
   b. Fill the bags with spa water from the maximum, medium, and minimum depths 30 cm below surface and 1 m from edge without leaving air pockets in bags to prevent oxygen from getting into samples.
   c. Use sterile sampling bags to collect spa water samples to avoid contaminations per NIEA101.00T for total coliform and total colony forming unit (CFU) tests.
   d. In samples containing free chlorine, add a proper amount of sodium thiosulfate into the sampling bags (120 mL of water sample requires 0.1 mL, 10% sodium thiosulfate, which reduces 15 mg L^{-1} of free chlorine).
   e. Avoid air pockets when filling the sampling bottles to avoid oxygen contamination.
   f. During transportation and storage of samples, maintain a temperature of 0-5 °C.
   g. Incubate coliform and CFU tests within 6 h.
   h. Incubate in a sterile environment.

(3) Spa Water Bacteria Cultivation and Disinfection Experiments:
   a. Add proper amounts of chlorine dioxide to the collected spa water samples and mix thoroughly for 10 min to obtain chlorine dioxide concentration (as ClO_2) levels of 0 (background as control), 0.25, 0.5 and 0.7 mg L^{-1}.
   b. Repeat step (a) by adding proper amounts of sodium hypochlorite to the spa water samples and mix thoroughly to obtain sodium hypochlorite concentrations (as Cl_2) of 0 mg L^{-1} (background as control) and 1.8 mg L^{-1}.
   c. Prepare petri dishes by adding the spa water samples with and without disinfectants from Steps (a) and (b) to petri dishes and then measure total coliforms level and total CFU level.
   d. Monitor the pH level, free chlorine, conductivity, nitrate, nitrite concentrations.

RESULTS AND DISCUSSION

1. Analysis of Spa Water Characteristics

Table 1 gives the pH, conductivity, free chlorine, total free chlorine, nitrate, nitrite, and ammonia of water samples. The spa water has a temperature of 40 °C and a pH level of 6.6-7.7. Water conductivity depends on many factors, including chemical content, concentration level, and temperature; spa water has a conductivity of 0.53-0.63 mS cm^{-1}. According to Taiwan Water Resources Management Bureau Criteria, water with conductivity less 750 μS cm^{-1} is suitable for irrigation

Table 1. Analysis of spa water chemical quality (MEAN ± SD)

Items	Disinfectant			
	ClO_2 (mg L^{-1} as ClO_2)			NaOCl (mg L^{-1} as Cl_2)
	0.25	0.5	0.7	0.7
pH Range	6.5-6.8	6.3-6.9	7.5-7.9	7.1-7.4
Conductivity (mS cm^{-1})	0.53 ± 0.02	0.60 ± 0.09	0.63 ± 0.05	0.59 ± 0.00
Free Chlorine Residual Level	0.013 ± 0.001	0.013 ± 0.001	0.013 ± 0.020	0.909 ± 0.031
Total Free Chlorine Level	0.045 ± 0.031	0.038 ± 0.035	0.026 ± 0.033	0.106 ± 0.024
Nitrate Nitrogen (mg L^{-1})	0.33 ± 0.32	0.04 ± 0.03	0.01 ± 0.00	0.26 ± 0.07
Nitrite Nitrogen (mg L^{-1})	0.002 ± 0.001	0.003 ± 0.001	0.371 ± 0.146	0.009 ± 0.008
Ammonia Nitrogen (mg L^{-1})	0.23 ± 0.17	0.30 ± 0.20	0.17 ± 0.02	0.16 ± 0.19

Table 2. Application of chlorine dioxide disinfection in spa water

Disinfection time (h)	0.25 mg L^{-1} as ClO_2		0.5 mg L^{-1} as ClO_2		0.7 mg L^{-1} as ClO_2	
	ClO_2 Residual Level	Total CFU (CFU mL^{-1})	ClO_2 Residual Level	Total CFU (CFU mL^{-1})	ClO_2 Residual Level	Total CFU (CFU mL^{-1})
Background value	0.02	770	0.02	10100	0	1740
1	0.06	90	0.10	100	0.31	17
2	0.04	70	0.09	60	0.22	14
3	0.04	30	0.07	70	0.22	14
4	0.02	40	0.08	40	0.26	0
8	0.02	270	0.04	500	0.34	24
12	0.02	320	0.03	920	0.24	77
18	0.01	2110	0.02	1030	0.27	10

[8]. Thus, spa water is suitable for irrigation because it does not harm the crops or salinize the soil [8]. Usually, hot spa water is not chlorinated because high temperature chlorination produces chlorates that produce odors and makes it inappropriate for use in spas.

Indicators of water chemical quality include total organic nitrogen, ammonia, nitrate, and nitrite. High ammonia levels indicate recent contamination of the spa water by body waste such as sweat or urine. If the water mainly contains nitrate, the ammonia has been oxidized via nitrification; nitrite is then converted to nitrate. The Taiwan EPA standards (Class I) are currently 0.1 mg L^{-1} for ammonia nitrogen, 0.1 mg L^{-1} for nitrite nitrogen, and 10 mg L^{-1} for nitrate nitrogen [9]. Therefore, according to Table 1, the spa water does not meet the ammonia standard. However, it does meet the nitrate standard. Regarding the nitrite level, the spa water with 0.25-0.5 mg L^{-1} as ClO_2 and 1.8 mg L^{-1} as Cl_2 does meet the standards. However, after increasing the ClO_2 level from 0.5 to 0.7 mg L^{-1} the water no longer meets the standards.

2. Results for Disinfected Spa Water

Chlorine dioxide at various concentrations was used to disinfect the spa water. Table 2 shows the data for total CFUs. The background data (without disinfectant) were also provided to indicate the disinfection efficiency. The water quality standards issued by the Taiwan Centers for Disease Control (CDC) are < 500 CFU mL^{-1} for total CFU level and < 1 CFU 100 mL^{-1} for total coliforms level [7]. As Table 2 shows, disinfection of spa water with different ClO_2 levels cannot meet the CDC standards in terms of total CFU levels.

In laboratory testing, disinfectant concentrations must meet CDC standards for total CFU level within 8 h after disinfection. The corresponding efficiencies are 64.9% (770 to 270 CFU mL^{-1}) and 99.4% (10100 to 500 CFU mL^{-1}) for 0.25 and 0.5 mg L^{-1} ClO_2, respectively. However, the CFU values increased after 8 h of disinfection due to the decrease in the residual disinfectant concentration as also reported by others [10]. The re-growth may be due to the fact that some organisms have survive after disinfection by utilizing residual organics. Nonetheless, at 0.7 mg L^{-1} ClO_2 the disinfectant concentration, the corresponding efficiency after 12 h was > 95.6% (1740 to 77 CFU mL^{-1}) for the total CFUs. Table 2 clearly shows that increasing the ClO_2 level from 0.5 to 0.7 mg L^{-1} significantly increases residual ClO_2 levels.

Chlorine dioxide and sodium hypochlorite were used to disinfect the samples with results shown in Table 3. Again, the water quality standards issued by the Taiwan CDC are < 500 CFU mL^{-1} for total CFU level. For the spa water, the background level was 1740 CFU mL^{-1} for total CFU, exceeding CDC standards. After disinfection, treated spa water can meet the standards with corresponding concentration of 0.7 mg L^{-1} as ClO_2 or 1.8 mg L^{-1} as Cl_2. The corresponding

Table 3. SPA water disinfection test data

Disinfection time (h)	0.7 mg L^{-1} as ClO_2		1.8 mg L^{-1} as ClO_2	
	ClO_2 Residual Level	Total CFU (CFU mL^{-1})	Free Chlorine Residual Level	Total CFU (CFU mL^{-1})
Background value	0	1740	0	1740
1	0.31	17	0.05	24
2	0.22	14	0.11	17
3	0.22	14	0.05	94
4	0.26	0	0.08	87
8	0.34	24	0.10	13
12	0.24	77	0.10	87
18	0.27	10	0.12	183

efficiencies are 99.4% (1740 to 10 CFU mL^{-1}) and 89.5% (1740 to 183 CFU mL^{-1}) for chlorine dioxide and sodium hypochlorite, respectively.

Sodium hypochlorite as a disinfectant has several side effects. Sodium hypochlorite, which is weakly alkaline (9-12 pH), can cause skin irritation [11]. If swallowed, it can react with water and carbon dioxide to form sodium bicarbonate and hypochlorous acid. The hypochlorous acid then converts to oxygen and hydrochloric acid, which is corrosive. Moreover, the hydrochloric acid can interact with sodium hypochlorite to produce sodium hydroxide and chlorine gas, which is harmful to the respiratory system and can cause pneumonia. Sodium hypochlorite combined with ammonia generates monochloramine, which can interact with water to produce hypochlorous acid. Both monochloramine and hypochlorous acid are harmful to the respiratory system and can cause pneumonia [12-15]. Since sodium hypochlorite has many side effects, and its disinfection efficiencies are inferior to those of chlorine dioxide based on the data listed in Table 3, chlorine dioxide is clearly superior to sodium hypochlorite for disinfecting spa water.

The results in Table 4 indicate that chlorine dioxide and sodium hypochlorite have high failure rates in total CFU and total coliforms tests. This further demonstrates that spa pools require increased residual chlorine dioxide to meet microbiological standards. Residual chlorine concentrations that are too low cannot prevent the re-growth of bacteria and viruses. However, residual free chlorine concentrations that are too high can cause unpleasant odors, eye and nose irritation, and bleaching of the hair. Moreover, they can also produce chloroform, which is a carcinogen [17]. To avoid some of the drawbacks of using chlorine, chlorine dioxide can be used.

The results in this study show that compared to sodium hypochlorite, chlorine dioxide is generally a more efficient and safer disinfectant. As a spa disinfectant, chlorine dioxide is an effective and non-carcinogenic antibacterial [17]. Further, visitors must wash thoroughly before using herbal spas to avoid cross contamination. Resorts should routinely apply adequate ClO_2 disinfectant to disinfect herbal spas as required by Taiwan EPA standards. However, an effective biocide for microorganisms is still needed, especially for public pools, to limit the spread of infections among users.

CONCLUSIONS

1. Spa water with a temperature of 40 °C and a pH of 6.6-7.7 does not meet total CFU and total coliform standards.
2. The laboratory simulation results indicate that 0.7 mg L^{-1} ClO_2 disinfects the spa water samples for up to 18 h, which complies with Taiwan EPA standards.
3. Regarding total CFUs in spa water, the equivalent concentration required to meet the standards is 0.7 mg L^{-1} ClO_2 or 1.8 mg L^{-1} Cl_2. Chlorine dioxide and sodium hypochlorite have efficiencies of 99.4%

Table 4. Spa water microbiological test results

Chlorine dioxide Residual (mg L^{-1} as ClO_2)	No. of Samples	No. of Samples Passed		Combined Passing efficiency (%)
		Total CFU	Total Coliforms	
< 0. 10	0	0	0	–
0.11-0.20	31	26	31	84
0.21-0.30	43	37	43	86
0.31-0.40	8	7	8	88
0.41-0.50	6	6	6	100
> 0.51	2	2	2	100
Free Chlorine Residual Level (mg L^{-1} as Cl_2)	**No. of Samples**	**No. of Samples Passed**		**Combined Passing efficiency (%)**
		Total CFU	Total Coliforms	
< 0.10	43	29	43	67
0.11-0.20	26	16	26	62
0.21-0.30	11	9	11	82
0.31-0.40	5	4	5	80
0.41-0.50	3	3	3	100
> 0.51	1	1	1	100

(1740 to 10 CFU mL^{-1}) and 89.5% (1740 to 183 CFU mL^{-1}), respectively. These data showed that the disinfection efficiency of chlorine dioxide is superior to that of sodium hypochlorite in terms of effects on total CFU. Therefore, ClO_2 is an excellent disinfectant substitute for NaOCl.

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