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Experimental Optimization of The Disinfection Performance of Sodium Hypochlorite and Hypochlorous Acid in Pilot and Industrial Cooling Towers

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Highlights

- The disinfection performance of Javelle water and chlorinated water in pilot and industrial cooling towers was evaluated;
- Due to the problems caused by the use of Javelle water, and especially its quality, which is very sensitive to light and heat and decomposes quickly, two substances, namely chlorinated water (hypochlorous acid) and Javelle water (sodium hypochlorite), were examined in pilot and industrial cooling towers;
- The experiments on the pilot tower showed that the performance of chlorinated water in the disinfection and removal of bacteria and microorganisms was excellent, and the total bacterial count (TBC) compared to Javelle water declined from 1000 to less than 800 (cfu/mL);
- The experiments on the industrial cooling tower of an acetic acid unit were also carried out for six months, and pH, free chlorine, and TBC were measured. Moreover, the results of process experiments and TBC tests confirmed the acceptable performance of chlorinated water.

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Abstract

Water can contain microorganisms and cause deposition and corrosion in cooling tower systems. Therefore, the water treatment of cooling towers is essential. Various biocides are used to remove bacteria and disinfect the water of cooling towers, and the most commonly used are sodium hypochlorite and chlorine compounds. This work examined two chlorinated water, namely hypochlorous acid and sodium hypochlorite, in two pilot and industrial cooling towers. The results of the experiments on the pilot tower showed that the performance of hypochlorous acid in the disinfection and removal of bacteria and microorganisms was excellent. The total bacterial count decreased from 10000 to less than 800 (cfu/mL) compared to sodium hypochlorite. The experiments were performed on the industrial cooling tower of an acetic acid unit for six months, in which pH, free chlorine, total bacterial count (TBC), and sulfate-reducing bacteria (SRB) were measured. The very high disinfection power of hypochlorous acid compared to sodium hypochlorite and its relatively lower pH level led to a significant reduction in the use of chemicals in the cooling tower. The experiments and TBC and SRB tests showed outstanding performance in using hypochlorous acid.

Keywords: Cooling tower, Hypochlorous acid, Sodium hypochlorite, TBC and SRB bacteria

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1. Introduction

One of the most widely used cooling tower types in the petrochemical industry is the open cooling tower system. In open cooling towers, air exchange with circulating water is crucial for heat transfer and cooling water. Due to a load of microbial contamination and the growth of bacteria and algae, it is essential to ensure that living organisms are killed and prevented from growing in the water of the cooling tower. The accumulation of microorganisms in water also causes the formation of biological layers and sediments on the cooling tower equipment, premature corrosion and erosion of equipment, blockage of pipes, and formation of insulation and thermal barrier coatings on heat transfer surfaces, reduce the efficiency of the cooling tower system. In industry, microbial corrosion damage accounts for about 20% of total corrosion damage (Dall'Agnol, 2014; Mazhar et al., 2020). Various compounds and microbicides of chlorine, bromine, chlorinated phenol, copper salts, and ozone kill and control microorganisms in cooling towers. The germicidal material is selected based on the cooling tower conditions economically. Ozone is a powerful disinfectant and an exciting alternative to chemical biocides in the water treatment of cooling towers. The use of ozone in cooling towers enjoys excellent advantages, such as safety and ease of use, low maintenance costs, and high efficiency and effectiveness. However, it has disadvantages, such as unsuitability for water with high hardness and chemical oxygen demand (COD), short storage time and low half-life of ozone, and reduced ozone solubility at high temperatures, limiting its use (Otson et al., 1986; Postigo et al., 2021; Srivastav et al., 2020). In some previous research, ultraviolet rays have been used to disinfect the water of cooling towers. The advantages of this method include avoiding chemicals and hazardous gases, eliminating the steps of transportation and storage, and reducing the cost of using chlorine gas (Kim et al., 2021). The most common method to kill microorganisms is to use biocides, which are often toxic and produce toxic and hazardous effluents. In addition to environmental issues, the use of chemicals imposes high costs on the system. In the past, environmentally harmful biocides were used. Over time and considering the strict environmental regulations, these biocides have been replaced by biodegradable and environmentally friendly biocides.

In 2013, the European Union banned PBD biocides and replaced them with environment-friendly biocides (Mazhar et al., 2020). Due to the ban on a wide range of metal and organic-based biocides, including formaldehyde, which is harmful to the environment, their use in cooling towers has been prohibited. Chlorine gas is more efficient in disinfection than other halogen oxidizing biocides (Prasadini et al., 2019). According to Simpson et al. (1993), the best-halogenated disinfectant is in the pH range of 6.8 to 9.3 and a load of microbial contamination, chlorine gas, and sodium hypochlorite. Studies conducted by Betz Dearborn also show that the best-halogenated disinfectants are hypochlorous acid and sodium hypochlorite. However, sodium hypochlorite decomposes rapidly and turns into salt due to its short half-life and high sensitivity to light and heat (Moore et al., 1991; Ghernaout, 2017). The formula for decomposing sodium hypochlorite is given by:

$$2NaClO \rightarrow 2NaCl + O_2 \qquad (1)$$

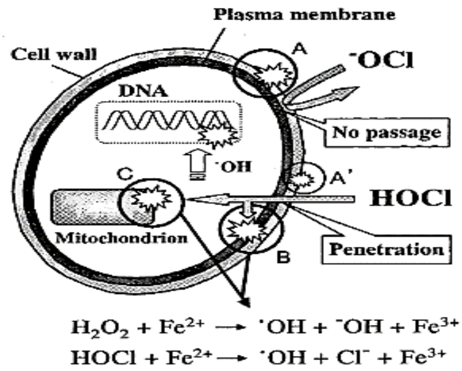
The most critical problem of using sodium hypochlorite, especially in hot seasons, is the storage of this material, and the consumer practically injects salt into the cooling tower instead of the disinfectant due to the distance of the manufacturing companies. Studies show that hypochlorous acid (HClO) is over 80 to 100 times more potent than sodium hypochlorite in killing bacteria and microorganisms. Further, Fukuzaki et al. (2007) investigated the effect of HClO and OCl^- and emphasized the strength of hypochlorous acid in disinfection operations. MAchmit et al. (2018) examined the effects of HClO and its disinfecting power; Walraven and Chapman (2016) examined various disinfection methods on cooling tower water and evaluated the advantages and disadvantages of disinfectants such as chlorination and UV. Wang et al. (2019) examined and compared chlorination and UV disinfection methods. The evaluation of corrosion and sedimentation of water at different pH values, total hardness, and calcium of water was performed by Amouei et al. (2017). Ukpaka et al. (2013) also studied and evaluated the corrosion and sedimentation rates and the effects of biocides on the industrial water-cooling tower in an olefin unit.

Many microorganisms in the water of cooling towers use the resulting hydrogen in their metabolic processes, leading to cathodic non-polarization of the corrosion reaction. The release of hydrogen from the surface of a metal on which microorganisms are located provides a means of perpetuating the corrosion reaction. Oxygen released by algae also contributes to the cathodic non-polarization of the corrosion reaction as a part of their metabolic changes. Quantitative analysis of a sediment sample also shows that microbial origin organic suspended solids from a part of the sediment. Aerobic bacteria convert ferrous oxide to ferric oxide and eventually iron hydrate, contaminating water by precipitation (Dall'Agnol, 2014).

$$4Fe(HCo_3) + 2H_2o + O_2 \rightarrow 4Fe(OH)_3 + 8Co_2 \quad (2)$$

Industrial studies show that chlorine and sodium hypochlorite are the most widely used disinfectants in circulating water for cooling towers today, considering that the process conditions and operation of each industrial cooling tower are specific according to the climate and the type of process of the petrochemical unit (Moore et al., 1991). Akpan et al. (2015) studied the disinfection effect of sodium hypochlorite on the disinfection of sulfate-reducing bacteria (SRB) anaerobic bacteria.

Fukuzaki investigated the disinfection effects of sodium hypochlorite and evaluated the disinfection rate of sodium hypochlorite (Fukuzaki, 2006).



Hashemi et al. (2019) studied the disinfection effect of perchlorine and sodium hypochlorite.

This work studies the disinfection and microbicide effect of hypochlorous acid and sodium hypochlorite in a pilot plant and industrial cooling tower with a maximum chloride content of 50 ppm, related to a petrochemical unit producing acetic acid. Most industries, such as petrochemical companies, have open cooling water systems for heat transfer, using sodium hypochlorite for disinfection.

2. Experimental procedures

The makeup water quality of both the pilot unit and petrochemical cooling tower (the acetic acid unit) is the same, and the water obtained from Fajr Petrochemical is of RO type. Table 1 lists the specifications of the inlet RO water of the cooling tower. Moreover, the process parameters and control range in both the pilot and petrochemical cooling towers are presented in Table 2.

Table 1
The specifications of the compensating water entering the cooling tower (RO water).

Constituent		Maximum Value	Unit
Total hardness	TH	7.8–8.2	ppm (as $CaCO_3$)
Calcium	Ca	25–50	ppm
Magnesium	Mg	<50	ppm
Sodium	Na	<2	ppm
Potassium	K	<1	ppm
Bicarbonate/carbonate	HCO_3	1.5	ppm
Sulfates	SO4	8	ppm
Chlorides	Cl	15	ppm
Nitrates	NO_3	0	ppm
Silica	SiO_2	0.2	ppm
TDS		38	ppm

Table 2
Process parameters and their control range in the cooling towers under study.

Parameter	Control range	Unit
pH	7.8–8.2	
Calcium (as $CaCO_3$)	25–50	ppm
Chloride (as Cl^-)	< 50	ppm
Total Fe	< 2	ppm
Total PO_4	6.6–7.6	ppm
Free chlorine	0.2–0.5	ppm
Total chlorine	1–1.5	ppm
Corrosion inhibitor	70–80	ppm
TBC	< 10000	ppm
M-Alkalinity	30–80	ppm
TSS	< 20	ppm
COD	< 50	ppm

2.1. Laboratory equipment

This work performed experiments on two cooling towers on the pilot and industrial scales. Air enters the tower reciprocally by induction suckers. The towers have polypropylene film fillers (FKP316/619).

The tower is made of three cells with the dimensions of each cell equal to 12 × 12 × 13.8 meters, and the total volume of the system is equal to 1500 cubic meters. The specifications of the industrial cooling tower of the acetic acid unit have been presented given in Table (3):

Table 3
The specifications of the industrial cooling tower of the acetic acid unit.

Specification	Value	Unit
Number of cells	3	
Design circulation water flow rate	7500	m^3/h
Actual circulation water flow rate	6500	m^3/h
Blow down flow rate	19	m^3/h
Number of fans	3	
Evaporation flow rate	141	m^3/h
Cooling water supply temperature	35	°C
Cooling water return temperature	45	°C

Figure 1 indicates the image of the pilot cooling tower.

Figure 1
The cooling tower of the pilot laboratory.

2.2. Testing method

HClO is produced by injection of hydrochloric acid according to the following reaction, which can combine with the enzyme of microorganisms and cause the disintegration of all organic and microbial materials.

$$Cl_2 + H_2O \rightarrow HCl + HClO \quad (3)$$

NaOCl is produced by injecting sodium hypochlorite into the cooling tower, killing microorganisms.

Industrial kits have been used to test the TBC and SRB bacterial count. The laboratory bacterial counting kit is for counting aerobic and anaerobic bacteria. In industrial waters, excessive accumulation of these bacteria leads to biofilms that may cause several technical problems in the system. The general detection of these bacteria and their counts in the water prevents their growth until the proliferation and formation of bulky biofilms. The total number of aerobic bacteria in a water sample can be determined using laboratory kits, and this kit contains a sterile culture medium layer for various bacteria in a sterile glass container. The TBC kit has been prepared based on the API standard and is used in many industries. Figure 2 shows the laboratory bacterial counting kit. The image on the right shows the culture medium before the growth of aerobic bacteria, and the image on the left shows the culture medium after the growth of aerobic bacteria.

Figure 2
Laboratory bacterial counting kit before and after bacteria culture.

Sulfate-reducing bacteria (SRB) is a group of anaerobic bacteria that produce hydrogen sulfide. This group of bacteria causes significant problems from the smell of rotten eggs to the blackening of equipment, water, the formation of sludge, and the beginning of the corrosion process. One of the most critical corrosion agents in the oil, gas, and petrochemical industries is corrosion caused by hydrogen sulfide gas. Many oil and petrochemical plants are made of carbon steel and are susceptible to corrosion by hydrogen sulfide gas. Hydrogen sulfide causes various types of corrosion in these steels. Detecting this microorganism is challenging due to its anaerobic nature and tendency to grow in biofilms and slow growth in conventional media. SRB kit is based on NACE and API reference standards.

Figure 3
Laboratory bacterial counting kit of SRB before and after the bacteria culture.

3. Results and discussion

3.1. Experiments on the pilot cooling tower

In this study, experimental tests were performed for one month in the pilot tower, and sodium hypochlorite was used as a widely used disinfectant in the industry; the free chlorine content in the system was controlled in the range of 0.3 to 1 ppm. A bacterial test was performed on the pilot cooling tower every 5 days. The results of bacterial counting and circulating water pH are listed in Table 4.

Table 4
The TBC and SRB counting and the pH of the circulating water in the pilot cooling tower with sodium hypochlorite.

Samples	Free chlorine (ppm)	pH	TBC (cuf/mL)	SRB (cfu/mL)
1	0.7	8.7	> 10000	> 10000
2	0.5	7.5	1500	1600
3	0.4	7.2	450	650
4	0.3	7.0	130	150
5	0.3	6.5	0	0

Then, hypochlorous acid was used as a disinfectant in isolated experiments for one month. The reaction of combining chlorine with water is as follows.

$$Cl_2 + H_2O \leftrightarrow HClO + H^+ + Cl^- \quad (4)$$

Experimental tests were performed regularly every 5 days, and the results of the TBC and SRB bacterial counting and the circulating water pH of the pilot tower are presented in Table 5.

Table 5
The TBC and SRB counting and the pH of circulating water in the pilot cooling tower with hypochlorous acid.

Samples	Free chlorine (ppm)	pH	TBC (cfu/mL)	SRB (cfu/mL)
1	0.40	7.3	4000	5000
2	0.32	7.2	1000	700
3	0.30	7.0	150	100
4	0.28	7.0	0	0
5	0.30	6.9	0	0

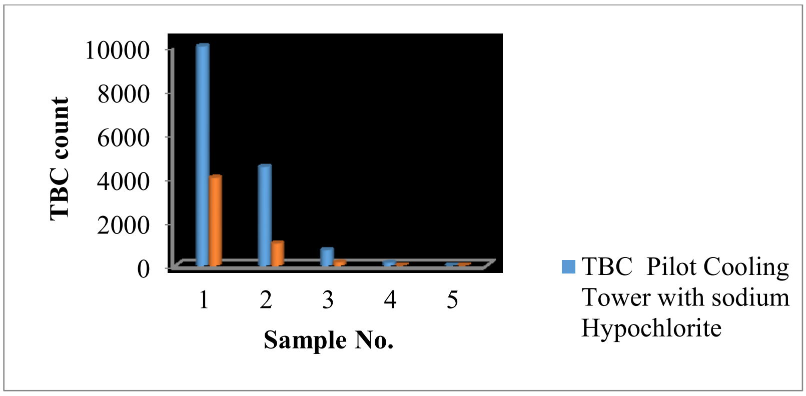


Figure 4
Comparing the TBC results obtained from the performance of sodium hypochlorite and hypochlorous acid in the pilot cooling tower in the same period.

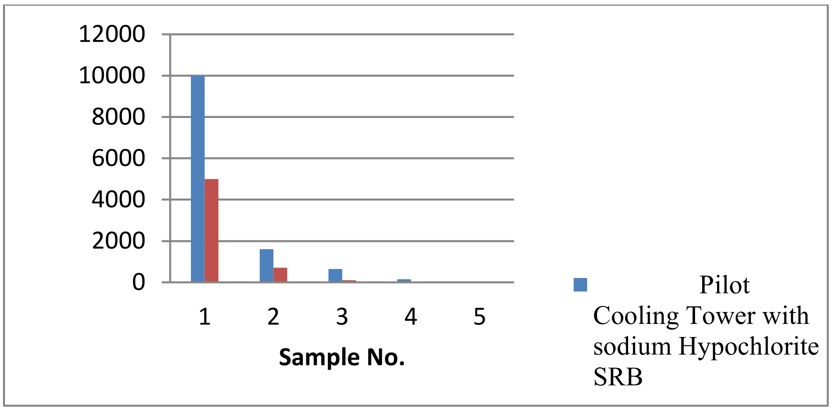


Figure 5

Comparing SRB results obtained from the performance of sodium hypochlorite and hypochlorous acid in the pilot cooling tower in the same period

The results of the experiments obtained from the disinfection of the pilot tower circulating water using hypochlorous acid (the production of hypochlorous acid solution) showed that the TBC and SRB bacterial tests were very satisfactory. In addition, due to the low pH of hypochlorous acid below 7.0, the pH of the circulating water did not increase. It should be noted that the approved standard values for the TBC and SRB below 10000 and below 1000 are excellent conditions for industrial cooling towers (Walravenand Chapman, 2016).

3.2. Experiments on the industrial cooling tower of acetic acid unit

Because sodium hypochlorite water is used for the disinfection of the cooling tower of the petrochemical unit, like other cooling towers in the industry, this study performed experimental tests for six months in the industrial cooling tower of the petrochemical unit. Sulfuric acid was used, and sulfur was the feed of SRB bacteria to maintain the pH of the system within the control range of the design. After the experiments, the results of bacterial count (TBC) and the pH of circulating water are presented in Table 6.

Table 6

The TBC and SRB counting and the pH of the circulating water in the industrial cooling tower of the acetic acid unit with sodium hypochlorite.

Samples	Free chlorine (ppm)	pH	TBC (cfu/mL)	SRB (cfu/mL)
1	0.85	8.7	< 10000	< 10000
2	0.80	8.3	5000	4500
3	0.40	7.2	1000	800
4	0.34	7.0	0	100
5	0.30	6.5	0	0

Moreover, we performed experimental tests on the circulating water of the industrial cooling tower of the petrochemical unit. Hypochlorous acid was used as a disinfectant for one month in separate experiments. In these experiments, pH, free chlorine, TBC, and other process parameters of each shift (8 h) were measured, and the results of pH, free chlorine, and TBC of several circulating water samples are tabulated in Table 7.

Table 7
The experimental tests for TBC and SRB counting and the pH of the circulating water in the industrial cooling tower of the acetic acid unit with hypochlorous acid.

Samples	Free chlorine(ppm)	pH	TBC (cfu/mL)	SRB (cfu/mL)
1	0.50	8.5	4500	2500
2	0.40	8.2	1500	1000
3	0.35	7.8	500	550
4	0.30	7.6	0	50
5	0.28	7.2	0	0

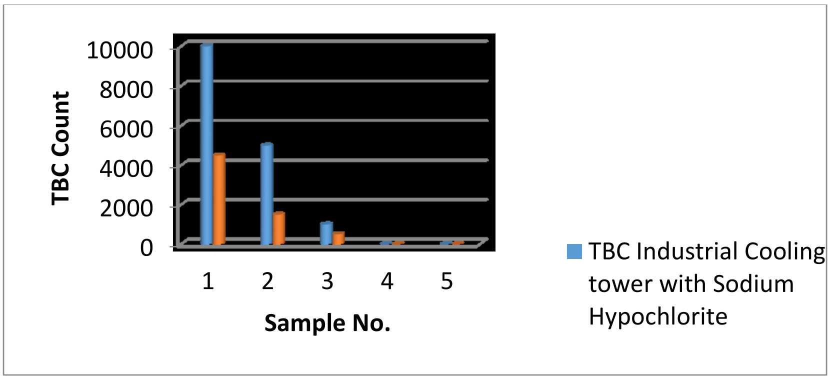


Figure 6
Comparing the TBC results obtained from the performance of sodium hypochlorite and hypochlorous acid in an industrial cooling tower in the same period.

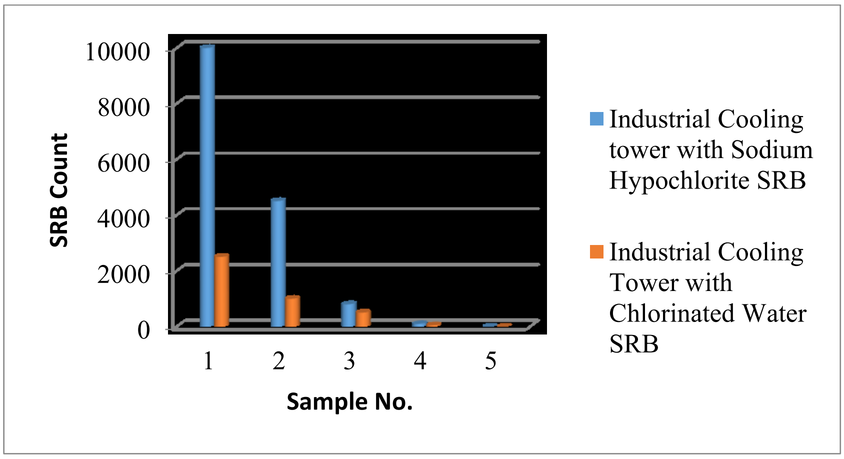


Figure 7
Comparing the SRB results obtained from the performance of sodium hypochlorite and hypochlorous acid in the industrial cooling tower in the same period.

It should be noted that during the use of hypochlorous acid, the pH of the water circulating of the cooling tower did not increase. Therefore, there was no need to inject sulfuric acid to adjust the pH. The comparison of the results of using hypochlorous acid in the pilot tower and the industrial cooling tower of the acid unit showed that the pH of the circulating water did not increase and was in the range of 7.0 to 8.5, and the acid consumption to adjust the pH reached zero. Nevertheless, most importantly, the microbial status of the tower was controlled, which resulted in good conditions compared to the consumption of sodium hypochlorite water for microbial control; the results of TBC and SRB were also all within the normal range. Another critical point is the microbial control in the range of low chlorine concentration compared to the time of using sodium hypochlorite. Therefore, considering the importance of microbial control and attention to high concentrations of free chlorine, one of the causes of chemical corrosion, system maintenance costs are reduced while achieving and ensuring safe disinfection by injecting hypochlorous acid. Sodium hypochlorite activity decreases by UV and heat, so NaClO converts to NaCl and O_2 by this reaction.

$$2\mathrm{NaOCl} \rightarrow 2\mathrm{NaCl} + \mathrm{O_2} \tag{5}$$

4. Conclusions

There are numerous process, operational, and economic problems with using sodium hypochlorite in industrial cooling towers, and there is a lack of quality sodium hypochlorite, especially in hot seasons in tropical regions with ambient temperature above 35 °C in more than 70% of the year. Furthermore, the half-life of the decomposition of sodium-hypochlorite water is smaller than 48 h at about 35 °C, so it is susceptible to light and heat. The results of using hypochlorous acid in pilot and industrial cooling towers indicate that using hypochlorous acid with high disinfection power, 80 to 100 times more potent than sodium-hypochlorite water, reduces industry costs due to energy consumption. Due to microbial corrosion and chemical consumption, hypochlorous acid compensates for water and chemicals such as corrosion inhibitors and scale dispersants. Disinfection with chlorine depends on pH; therefore, when pH is less than 7.0, active chlorine kills bacteria, and when the pH of the cooling water system increases to above 7.0, disinfection efficiency quickly decreases.

Nomenclatures

BC	Total bacteria count
PBD	Products biocide directive
TBC	Total bacterial count
SRB	Sulfate-reducing bacteria

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