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Full Length Research Paper

Free chlorine residual content within the drinking water distribution system

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This paper explains the principle of chlorination and reveals the free chlorine residual content within a drinking water distribution system located in peninsular Malaysia. The study found that the free chlorine at user points was slightly greater than 0.3 mg/l, which is higher than the WHO standard at 0.2 - 0.3 mg/l. Despite that it was not a guarantee to lower the level of the microbial since the results showed that the total coliform count was higher than the level suggested by Malaysian Water Association. Therefore, the tap water at the in-take point cannot be used for direct consumption but additional treatments such as filtration and boiling are required.

Key words: Drinking water distribution system, free chlorine residual, coliform.

INTRODUCTION

Although Geldreish (1996) has reported the free chlorine residual between 1.2 mg/L to 0.3 mg/L that can control the number of microbial at below 100 and 500 for every milliliter sample, drinking water distribution system (DWDS) in the tropical country should be treated as a unique case because of the climate. The temperature around 25 - 35^{o}C is quite optimal for most microbes to grow and it also increases the chlorine evaporation rate that reduces the hypochlorous acid in the equilibrium reaction. The hydrochlorous acid is the hydrolyzed form of chlorine in aqueous with strong capability of killing wide spectrums of pathogens. Strong sunlight also reduces the hypochlorate stability by photo-degradation process (Nowell and Hoigne, 1992). Moreover, heavy rainfall received every year at 1000-2000 mm also affect the consistency of water treatment system operation. This study discussed the chlorination process principle and reveals the free chlorine residual within a drinking water distribution system located in Peninsular Malaysia.

Theory

The chlorination process in the DWDS has been practiced in many countries to encounter the water bone diseases. It also useful as a disinfections agent, odor removal, algae re-growth protection,bleaching agent, increases coagulation of the activated silica and prevents the re-growth of the microbial (White, 1992). The superior advantages of the chlorine compared to other halogens chemicals such as bromine, and fluorine as disinfectant, well-understood of its side effects to the human life. Besides, easy to store and transport, competitive price, continuous prevention of microbial re-growth, and gives the most effective property to control varied pathogen spectrums.

Despite the chlorine properties that can control the water bone diseases, its side effects required regulations and standards to limit to a minimum level. World health organization (WHO, 1993) set the free chlorine residual in drinking water should be around 0.2 - 0.3 mg/L for 30 min contact time. The drinking water safe act 1974, amendment 1986 (SWDAA) outlines that the free chlorine should be less than 0.2 mg/L at any delivery points. Since the pioneering work of Rook (1974), many investigations have also been conducted in the formation and the precursors of chlorination disinfection by-products (CDBPs) (Blatchley, 2003; Ge at al., 2006). Chlorine in water combines with natural organic compounds NOM to yield a large range of CDBPs such as trihalomethanes (THMs), haloacetic acids (HAAs), chlorophenols, phenolic acids, chlorinated quinines exhibits potentially carcinogenic, teratogenic and mutagenic activities to hu-

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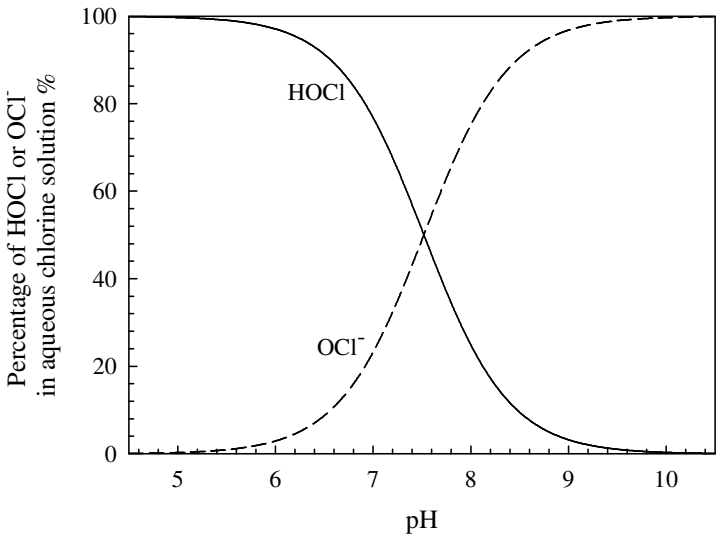

Figure 1. Dependence of the ratio HOCl/OCl^- on pH (pK_a = 7.5).

man health (Yang and Shang, 2004). Therefore the United State Environmental Protection Agency (USEPA) (1994) has set the THMs must not greater than 0.1 mg/L at the intake point.

Chemistry of the chlorine equilibrium

Henry rule gives the equilibrium of chlorine in water as:

$$Cl_2(aq) \Leftarrow\Rightarrow Cl_2(g) \quad (1)$$

Since the evaporation of chlorine is minimal, aqueous chlorine is hydrolyzed as below;

$$Cl_2 + H_2O \Leftarrow\Rightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \Leftarrow\Rightarrow H^+ + OCl^- \quad (3)$$

Hypochlorous acid (HOCl) is also less evaporates at 1.28 x 10^5 to compare with chlorine gas (Blatchley et al. 1992).

$$K = \frac{[H^+][Cl^-][HOCl]}{Cl_2} = 4x10^{-4} \quad (4)$$

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} \quad (5)$$

The equilibriums of the chlorine in the form of Cl_2, HOCl and OCl^- depend on the pH and temperature. Morris (1966) studied the temperature effect and gives the empirical equation below;

$$pK_a = \frac{3000 - 10.068 + (0.0253)T}{[Cl_2]} \quad (6)$$

Where T in Kelvin, and *pKa* is equilibrium constant.

According to the equilibrium of reaction 3, more than 99% of the free chlorine is HOCl at pH 5 and similarly more than 99% is OCl^- at pH 10. Figure 1 shows this relation graphically. The HOCl is 80 to 200 times stronger than OCL^- in-term of disinfecting the pathogens (White, 1992)

Organic and inorganic reactions

The organic and inorganic compounds can be ammonia, nitrite, nitrate, amino acid, and suspended solids. When hypochlorous acid reacts with organic compounds, the disinfections capability of the HOCl becomes weak. The reactions are as follow;

$HOCl + NH_3$ ----------> $NH_2Cl + H_2O$
$NH_2Cl + HOCl$ ----------> $NHCl_2 + H_2O$
$NHCl_2 + HOCl$ ----------> $NCl_3 + H_2O$

Others reactions are such as;

a) Carbon

$C + 2Cl_2 + 2H_2O$ ----------> $4HCl + CO_2$

b) Cyanide

For pH 8.5 or more

$2Cl_2 + 4NaOH + 2NaCN$ --------> $2NaCNO + 4NaCl + 2H_2O$
$5Cl_2 + 10NaOH + 2NaCN$ --------> $2NaHCO_3 + 10NaCl + N_2 + 4H_2O$.

c) Hydrogen Sulfide

$H_2S + 4Cl_2 + 4H_2O$ -------> $H_2SO_4 + 8HCl$
$H_2S + Cl_2$ ----------> $S + H_2O$

d) Ferrous
$2Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)_2 \text{ ---------> } 2Fe(OH)_3 + CaCl_2 + 6CO_2$

e) Manganese
$MnSO_4 + Cl_2 + 4NaOH \text{ ---------> } MnO_2 + 2NaCl + Na_2SO_4 + 2H_2O$

f) Methane
$CH_4 + 4Cl_2 \text{ ----------> } CCl_4 + 4HCl$

Disinfections kinetics

Chick (1908) proposed the kinetic of organism disinfections by the first order;

$$\frac{dN}{dt} = -kN \quad (7)$$

Where N is the numbers of microorganism, t is time and k is death rate. Watson (1908) studied the coefficient of disinfections and proposed;

$$k = \alpha C^n \quad (8)$$

Where C is disinfections concentration, n constant of others solutions and α deactivated constant. Combining the two equations becomes the Chick-Watson model.

$$\ln \frac{N}{N_o} = -\alpha C^n t \quad (9)$$

Where No = numbers of microorganism in early stage. The Chick-Watson model is well accepted to represent the disinfections kinetic in water system.

Chlorine decay in the water treatment system

Teefy and Singer (1990) proposed the free chlorine decay rate in the water treatment system by the first order reaction with k ranging from 0.162 to 0.0624/h. Lawler and Singer (1993) suggested that 0.2/h is an acceptable retention time. Gawad and Bewtra (1988) proposed that the free chlorine residual during the physical-chemical treatment for river water is also a first order reaction. In addition, they also included the tabular flow, evaporation, photolysis, and temperature in their equation.

$$K_T = F_{TB}(K_{ev} + K_s + K_{ox})\theta^{(T-20)} \quad (10)$$

Where K_T is the coefficient rate at temperature T, F_{TB} tabular factor, K_{ev} evaporation constant, K_s rate of photo-oxidation, K_{ox} oxidation of free radical of chlorine, θ arrhenius constant, T temperature (°C), F_{TB} = 2.05 for tabular flow and 1.0 for laminar flow; K_{ev} = 0.013/H d^{-1} (H dept of flow in meter); K_s = 0.03 d^{-1} ; K_{ox} = 0.065 d^{-1} and θ = 1.08.

Nowell and Hoigne (1992) reported that the photo-degradation of the chlorine is the first order reaction and found that the hypochlorate ion is more sensitive to the sunlight then the hypochlorous acid.

Chlorine decay along DWDS

Calculating the decay rate of free chlorine in many input and many output (MIMO) networks piping system of the DWDS is a great challenge. The date should be associated with hydraulic study such as flow rate, flow pattern, networking, contour, pipe sizing, and retention time, age of the system, and the distances as well. In general, Eular and Lagrange are the two models that able to define numerically the free chlorine residual within the system.

The Eular technique applies the finite different method (FDM) by dividing the pipe into the segments at the same volume. Chaundhry and Islam (1994) proposed the partial derivative technique to estimate the chlorine decaying in a single pipe as;

$$\frac{\partial c(x,t)}{\partial t} + v\frac{\partial c(x,t)}{\partial x} = Kc(x,t) \quad (11)$$

Where, $c(x,t)$ is the concentration of free chlorine at node x, v the velocity of water, and K the reaction order. By assuming a complete mixing in every junction, the chlorine residual model proposed by Rossman et al. (1993, 1994) and Rossman and Boulos (1996) can estimate the concentration of the free chlorine. For a single pipe, Rhee et al. (1986) proposed an exact solution for equation (10) as;

$$c(x,t) = \begin{cases} c(x - vt)\, exp(-kt) & \text{for } x - vt > 0 \\ c(0,\ t - x/v)\, exp(-kx/v) & \text{for } x - vt < 0 \end{cases} \quad (12)$$

Zierolf et al. (1998) developed the DWDS input-output (I-O) model to express the chlorine concentration at the pipe junction and time as a weighted average of exponentially decayed values of the concentrations at all adjacent upstream junctions. In the Lagrange model, the chlorine residue mass balance that entering the system will be simultaneously detected and recorded (Propato and Uber, 2004). This technique is also classified as the time driven method (TDM). Boulos et al. (1994) was also successfully explained the event driven method (EDM).

MATERIAL AND METHOD

Drinking water distribution system

The DWDS of the Universiti Kebangsaan Malaysia (UKM), located in Bangi, Selangor, Malaysia was used as the drinking water networking system. The water is supplied by Semenyih treatment

Table 1. Water quality of semenyih dam at temperature (29 – 33)°C.

	Limits (MWA)	Minimum	Maximum	Average	Standard Deviation
PH value	6.5-9.0	6.0	7.7	6.8	0.2
Turbidity (NTU)	<5	25	56	40	2.5
DO (mg/L)	-	2.5	3.0	2.7	0.1
SS (mg/L)	<1000	-	-	-	-
COD (mg/L)	-	6.7	9.2	8.4	0.4

plant located about 45 km from UKM. The DWDS of UKM investigated included the pipe networking, three storage tanks, and five intake points (green house, staff quotas, kamsis c, mosque, and engineering department), with the covering area within three kilometers distance. The pipe ages ranging from 26 years to 4 years, while the diameters of pipes are 15 inches for main entrance and 12 to 6 inches in the network system.

Sampling points and method

Water samples were taken at Semenyih treatment plant's outlet, main entrance pipe to UKM network system, storage tank no 1, storage tank no 2 and user points. In-situ and grab methods were performed according to the standard accepted by APHA and USA National Primary Drinking Water regulations. All date points were repeated three times and were carried for three consecutive days.

In –situ measurements

Temperature measurements using thermometer, pH using equipment HACH model EC10, S/N 961100004617, turbidity using HACH model 2100P, S/N 980600018256 and reading in unit NTU (nephelometrik turbidity unit), dissolve oxygen using HACH model DR/2010 spectrophotometer, S/N 970600003879 and the value in unit mg/L, suspended solids using HACH model CO150, S/N 970500004016 and in unit of mg/L.

Measuring the COD

All samples were analyzed of the chemical oxygen demand performed according to USEPA's effluence monitoring procedures and guideline or the latest edition of standard methods for the examination of water and wastewater using ferrous ammonium sulfate (FAS) standardized to 0.25 N (as titrating reagent) against the ferroin indicator. The COD values were calculated according to the formula.

$$COD = \frac{(\text{blk} - \text{Sx}).(\text{N}_{\text{fas}}).(8.0\text{mg/meq wt}).(1000\text{mL/Liter})}{\text{Volume of sample (mL)}}$$

Where; blk = ml of FAS to neutralized the blank
Sx = ml of FAS required to neutralized the sample
Nfas = the standardized normality of the ferrous ammonium sulfate.

Measuring the free chlorine residual

Assessment of the free chlorine was carried out using spectrophotometer and Diethyl-P-Phenylenediamine (DPD) methods (Methods for examination of water and associated materials 1980). The reagent pillow was supplied by HACH, DREL/2010 that is equivalent to the standard methods 45000-CIG for drinking water by USEPA. Spectrophotometer type HACH model DR/2010 S/N 970600003879 was used.

Measuring the coliform

Two conventional methods of determining the coliform in drinking water are; the most probably numbers (MPN) and the filtration method (Gerard et al., 1995). The filtration technique was selected due to its ability of spreading the colonies and low suspended solid in the samples.

Using the standard aseptic technique, 100 ml sample was taken from the sampling points. Samples were filtered under vacuum and the filtrate was transferred onto the Eosin Metilline Blue agar (EMB) plate. EMBs were incubated for 24 h at 38°C. Black head or shining metallic would appear if the colonies presented. Direct counting of the colony was performed.

RESULTS AND DISCUSSIONS

Water source quality

Water source was tested at Semenyih Dam and the result is shown in Table 1. It was also compared to MWA's standard.

It can be seen that the COD value is greater than 8.33 mg/L, thus the dam is polluted, therefore, the water required the standard treatment system that consists of coagulation, flocculation, sedimentation and filtration. Since the COD was high, special treatments for organic removal may be required.

The free chlorine concentration when leaving the water treatment system (upon the water enter the distribution system) was tested as shown in Table 2. The results show that the average free chlorine concentration was at 3.58 mg/L. Comparing to WHO (1993) standard, this brought to conclusion that the water treatment plant during the day of the test was either overdosed or not enough contact time due to high demand. The pH was also low while other parameters were found within the limits as shown in Table 2.

Free chlorine residue concentration

The chlorine residual concentration was tested at phase

Table 2: Water test result at outlets of Semenyih treatment plant. The ambient temperature was 31 – 33°C.

	Limits	Minimum	Maximum	Average	Standard Deviation
Free Chlorine (mg/L)	0.2-0.3	3	4	3.58	0.25
pH value	6.5-9.0	5.7	6.1	5.78	0.02
Turbidity (NTU)	<5	0.39	0.8	0.41	0.05
DO (mg/L)	-	3.1	3.6	3.3	0.10
SS (mg/L)	<1000	20	40	31	2.60
COD (mg/L)	-	1.2	2.5	1.8	0.05

Table 3. Free chlorine residual content

	Distance from WTS (Semenyeh) KM	Pipe size and aging	Minimum	Maximum	Average	Standard Deviation
Bandar Baru Bangi storage tanks (2 & 4 million gallons)	37	42 in >35years	-	-	-	-
Main Entrance Pipe	44	15 in >26 years	0.47	0.64	0.53	0.01
Inlet to the storage tank (one million gallon)	46	15 in >26 years	0.43	0.61	0.50	0.15
Outlet from storage tank (one million gallon)	46	12 in >26 years	0.19	0.45	0.34	0.12
User points						
1. Green house	46.35	6 in	0.18	0.44	0.33	0.01
2. Staff Quotas	47.2	6 in	0.17	0.41	0.31	0.02
3. Kamsis C	46.9	6 in	0.17	0.41	0.31	0.02
4. Mosque	47.3	6 in	0.15	0.37	0.28	0.03
Average of Intake points.			**0.17**	**0.41**	**0.31**	0.04

one and two of the Universiti Kebangsaan Malaysia drinking water system and the results are shown in Table 3. As has been mentioned in the free chlorine test leaving the treatment plant was high at 3.58 mg/L, the free chlorine residual before entered the UKM drinking water distribution system was also high at 0.53 mg/L which is two to three folds higher then the WHO standard. The result also showed that the free chlorine residual dropped almost 7 folds than the free chlorine residue concentration when leaving the Semenyih's water treatment. Since the distance between the treatment plant and the UKM's water network system is quite far (about 45KM), this result confirmed that the chlorination process in the Semenyih treatment plant was insufficient of contact time and was overdose.

At inlet and outlet of the storage tank, the free chlorine residue concentrations dropped from 0.5 to 0.34 mg/L. The free chlorine residue continuously decayed to around 0.3g/L at the user point.

Total coliform count

According to the Malaysian Water Association (1994), the standard sampling practice of the drinking water in the distribution system should be;

All samples should be less than 10 coliform per 100 mL sample.
2. All samples should be free from *Escherichia coli*
3. The coliform should be not detected simultaneous.
4. In a year, at least 95% of samples free from coliform.

The data of total coliform is shown in Table 4. The results showed that all intake points gave over limit than the MWA standard. Since the test was carried out to follow the network stream, from the main entrance of the system until the user points, the numbers of microbial were increased. The highest level was 16 colonies per 100 ml samples at the mosque tap water. This result suggested that the microbial might be multiplied along the DWDS system mainly at the old piping system (Kamsis C and Mosque).

Conclusion

In this work, the free chlorine residual and microbial re-growth was investigated within the tropical climate of the DWDS. The chlorination process attributes as the disinfection agent and prevents the re-growth of microbial was found to be unsuccessful. Furthermore, a high free chlorine residue concentration at the treatment plant and the

Table 4. Total coliform colonies for every 100 ml sample.

	Colonies/100 mL			
	Low	**Minimum**	**Maximum**	**Standard Deviation**
Main Entrance Pipe	0	2	1	0.1
Inlet to the storage tank (one million gallon)	0	5	2	0.3
Outlet from storage tank (one million gallon)	0	9	4	0.2
Intake points				
1. Green house	1	8	4	0.1
2. Staff Quotas	2	9	5	0.2
3. Kamsis C	2	12	7	0.1
4. Mosque	2	16	9	0.3

intake point was not guaranteed to eliminate the microbial, therefore, the tap water at the intake point is not suitable for direct consumption but additional treatments such as filtration and boiling are required.

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