CHLORINATION AND CHLORAMINES FORMATION

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Abstract

Chlorination is the most important method of disinfection in Malaysia which aims at ensuring an acceptable and safe drinking water quality. The dosing of chlorine to surface water containing ammonia and nitrogen compounds may form chloramines in the treated water. During this reaction, inorganic and organic chloramines are formed. The recommended maximum acceptable concentration (MAC) for chloramines in drinking water is 3000 µg/L. The production of monochloramine, dichloramine and trichloramine is highly dependent upon pH, contact time and the chlorine to ammonia molar ratio. The purpose of this study is to examine the formation of chloramines that occur upon the chlorination during the treatment process. Chloramines were determined using the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method. The influences of ammonia, pH and chlorine dosage on the chloramines formation were also studied. This paper presents a modeling approach based on regression analysis which is designed to estimate the formation of chloramines. The correlation between the concentration of chloramines and the ammonia, pH and chlorine dosage was examined. In all cases, the quantity of chloramines formed depended linearly upon the amount of chlorine dosage. On the basis of this study it reveals that the concentration of chloramines is a function of chlorine dosage and the ammonia concentration to the chlorination process. pH seems to not significantly affect the formation of chloramines.

Keywords: Chlorination, chloramines, ammonia, chlorine dosage

Introduction

Disinfection involves the oxidation of organic and inorganic substances and the elimination of bacteria and viruses in the drinking water [1]. Chlorination of drinking water has been successfully used to deactivate the harmful microorganisms and is the most widely used method of disinfection in Malaysia today. Chlorination has virtually eliminated serious waterborne outbreaks such as dysentery, cholera and typhoid fever. Chlorine is the most widely used disinfectant because it is readily available, cost effective, easily applied and is more efficient than other disinfectants agents such as ozone, chlorine dioxide and potassium permanganate [2]. The formation of chloramines is adequately described using reaction involving aqueous chlorine and ammonia. The presence of nitrogenous organic compound in raw and treated water could cause problems as chloramines are formed, which also have some disinfecting power [3]. In general, the reactions are governed by two parameters: pH and the ratio of chlorine to ammonia. Chloramines as a disinfectants by-product, however offer several advantages such as reduction of the formation of trihalomethanes, increased residual activity in the distribution systems, reduction of odour and taste problems and control of bacterial biofilm regrowth in the distribution systems [4].

Chemistry of chloramines formation

Previous researchers have studied the influences of pH, ammonia concentration, chlorine dosage, reaction time, as well as the precursor type and precursor concentration on the formation of chloramines [5]. In aqueous systems, chlorine (Cl) reacts with ammonia (NH_3) to form chloramines. When chlorine is added to water, it proceeds through a series of reactions. Chlorine will first react with organic materials and metals in the water, and it is not available for chlorination. This is called the chlorine demand of the water [6]. When chlorine is used in the water treatment systems, it is added in either a gaseous or liquid form of chlorine. Chlorine hydrolyzes very rapidly and produces hypoclorous acid (HOCl) and hydrochloric acid (HCl) as described below:

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl$$

As pH varies in a system so does the concentration of hypochlorous acid versus the concentration of hypochlorite ion. Both HOCl and OCl are good disinfecting agents, but HOCl is more effective. Hypochlorous acid is a week acid that ionizes at pH 7.5 and 25 °C [7].

$$HOCl \leftrightarrow H^+ + OCl^-$$

The hypochlorous acid will react with ammonia in the water and form chloramines, which as mentioned earlier are a benefit due to their strong residuals and because when chlorine is converted to chloramines the formation of disinfection-by-products ceases. However, the chloramines are not very effective against viruses and are a weaker disinfectant. Hypochlorous acid reacts rapidly with ammonia to form monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or nitrogen trichloride (NCl_3) as shown in reactions below:

$$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O$$
$$NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O$$
$$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$$

The equations above are simplified to illustrate the complex effect of the chlorine-to-ammonia ratio on chloramines formation [8]. The reactions are equilibrium indicating that both forward and reverse reactions occur to an appreciable extent. The reverse reactions also indicate that if chloramines are dissolved in the water, chlorine and ammonia will be generated. In the real-world sample, chloramines chemistry entails a complex series of reaction involving many species, pathway and mechanism [9]. In short, free chlorine, nitrogenous compound and chloramines are chemically related and can be converted into each other.

Experimental

Description of water treatment plant

In this study, Semenyih river Water Treatment Plant (SRWTP), which supplies the water needs of more than 1 million inhabitants and is operated by Konsortium Abass Sdn Bhd was selected for the sampling source. SRWTP receives raw water from the Semenyih basin, which is the sub-basin of Langat river basin. SRWTP is located in Precint 19, Purajaya, Malaysia. It is one of the largest water treatment plant in Malaysia and has an average treated water production of about 140-145 million gallons per day (mgd). The development of new township in the basin such as Dengkil, Semenyih, Nilai and Rinching town attract people to the basin from other parts of the country to take the advantage of infrastructure and social and industrial employment. The SRWTP was design to produce quality water complying with drinking water standard. The water treatment processes involved in SRWTP are coagulation, flocculation, sedimentation, filtration, fluoridation and chlorination as shown in the Figure 1

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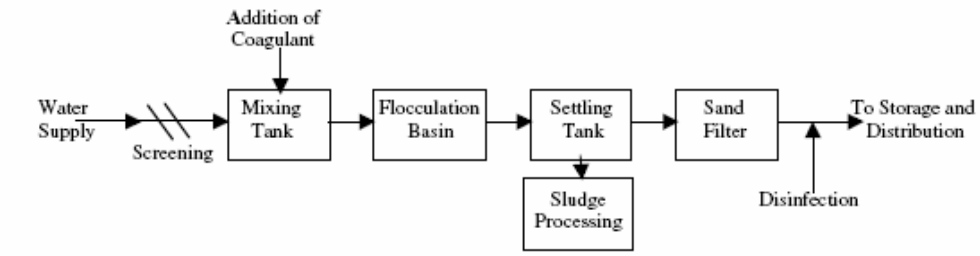

Fig. 1: Schematic of SRWTP water treatment processes

In this study, there were only two main sampling points along the processes of the water treatment plant. These were filtered water and treated water, which are the sample before and after the chlorination process. The study was carried out from March to September 2006.

Sample handling and pre-treatment

The samples before and after the chlorination process were carefully transferred to the laboratory in a cool box and stored in refrigerator at 4 °C to minimize changes in the constituents. During the sampling, the glass bottles were filled without passing air bubbles through the sample. The bottles were previously dipped in sulphuric acid,

washed with detergent, rinsed with deionized water and placed in an oven at 200 °C. Once the samples were collected, samples were carried to laboratory for analysis.

Analytical procedures and data collections

Chlorine residuals in the water sample were determined with both the DPD (*N,N-diethyl-p-phenylenediamine*) titrimetric and colorimetric method. In this method, DPD is used as an indicator with ferrous ammonium sulphate (FAS). Free chlorine, monochloramine, dichloramine and nitrogen trichloride were determined by adding the different amount of potassium iodide (KI). The wavelength used in the spectrophotometer was at 515 nm. The concentration of the each chlorine residuals was determined by calculation according to the established procedure [10] .

Ammonia nitrogen was determined with the Nessler method. The test was using by HACH spectrophotometer DR 2000. In this method, Nessler reagent (K_2HgI_4) reacts under alkaline conditions with the ammonia present in the sample to produce a yellow-colored species. The wavelength is set at 425 nm [11].

Due to the rapid chemical changes during transportation and storage, pH was measured onsite, immediately after the sample was taken. The chlorine dosage applied as the sum of pre-chlorination and post-chlorination was obtained from SRWTP.

Model development

The relationships between formation of chloramines and ammonia, pH and chlorine dosage were examined by simple correlation. Multiple regression analysis was then applied as a means to evaluate the significant variables of the formation of chloramines. The multiple stepwise regression was applied for the development of the linear model. Commercial software SPSS was used for the regression analysis. Stepwise regression can sequentially select and pick the important variables for a better simulation. The standard regression method enters all the input variables into the equation in one step, whilst stepwise method adds or deletes the variables from the model at every step of the regression until the best equation is generated.

Results and Discussions

Distribution of chloramine species in the treated water

The addition of chlorine to filtered water sample containing ammonia and organic nitrogen compound may form inorganic N-chloramines. Inorganic chloramines consist of monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and nitrogen-trichloride (NCl_3). Figure 2 shows the proportion of each residual chlorine species when free chlorine is added during the disinfection process. The result revealed that monochloramine was the principle chloramine that was encounter under the real chlorination conditions in the water treatment plant. The proportion of dichloramine and nitrogen trichloride was 7 % and 1 % respectively. Many reactions may occur between free chlorine and the complex mixture of organic constituents present in surface waters. The reactions which produce chloramines are dependent on the reaction time, pH, temperature and the relative concentrations of hypochlorous acid and ammonia, in addition to the chemical kinetics and equilibria for the many possible reactions. A regression model was employed to predict the relative amounts of total chloramines in the treated water. In this study, monochloramine was the most abundant chloramines formed. Hence the predictive model was best describing the formation of monochloramines. This helps to account for the formation of monochloramines in the disinfected water.

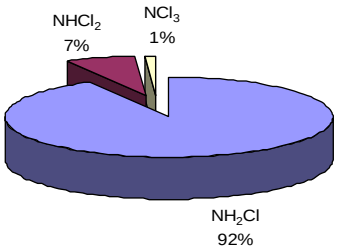

Fig. 2: Distribution of principal chloramine species in treated water

Pearson correlation test

Pearson correlation was conducted to determine the single measure of linear association between chloramines and the independent variables [12]. As expected formation of chloramines in treated water correlated with chlorine dosage and ammonia ($P < 0.001$). The output of the Pearson correlation is shown in Table 1 below.

Table 1: Correlation between the chloramines formation with the independent variables

Chloramines formation with independent parameters	Pearson Coefficient, r	P-value
Chlorine dosage	.663	.000
Ammonia	.836	.000
pH	-.176	.004

Using Pearson correlation method, a good relationship (r=.836) was obtain between the chloramines formation and ammonia concentration in filtered water. Samples with high concentration of ammonia presented higher chloramines formation. Nitrogenous compounds, especially amines and ammonia occur naturally in the surface water. Variations of these nitrogenous compound concentrations give substantial impact on the formation of chloramines. Chloramine is increasingly being used in the disinfection of drinking water. Many utilities practicing chloramination routinely add chlorine and ammonia at a ratio between 3 to 1 and 5 to 1. This showed that the creation of chloramines in potable water involving the addition of ammonia and chlorine. Hence, ammonia showed the best correlation with the formation of chloramines. In addition, the chloramines formation increased with chlorine dosage during disinfection. Chlorine acts as a potent oxidizing agent and often dissipates in side reactions rapidly that little disinfection is accomplished until amounts in excess of the chlorine demand have been added. Chlorine reacts with a wide variety of nitrogenous compounds to form chloramines. Thus, a medium and significant correlation was observed between the formation of chloramines and the chlorine dosage (r=.663, p=.000). However, a negative low but definite with small relationship (r=-.176) was obtained between chloramines formation and pH. In this study, the pH of the water samples ranged from 6 to 7. The pH value was persistently within this range throughout of the study. This is due the process of pH adjustment using lime before chlorination take place. Thus, pH is insignificant and not considered in the model development according to the logic of chlorination chemistry. The important role of pH nevertheless, does not necessarily preclude its involvement in chloramination reaction, if the pH changes dramatically.

Proposed model

Regresssion equation was developed in order to predict the chloramine formation [13]. Firstly, we found fair linear relationships linking the chloramines formation to each separate variables except pH. From the previous correlation test, a positive correlation was found between chlorine dosage, ammonia concentration and the formation of chloramine. Consequently, it is interesting to know if such a relationship is kept even though simultaneous influence from each variable. A general regression consists of three independent variables can be expressed as:

$$Y = A + B_1X_1 + B_2X_2$$

Where A is the constant of regression and B is the coefficient of the regression. Total chloramines are considered as dependent variables while ammonia concentration and the chlorine dosage are considered as independent parameters. R^2 was used to measure the goodness of fit of the model. It is defined as the proportion of the variation in the dependent variable.

The regression model obtained is as follows:

$$\text{Chloramine} = -0.031 + 0.552(\text{ammonia}) + 0.020(\text{chlorine dosage})$$

where all the units are expressed in mg/l. The model summary is shown in table 2 below. This model was found to be statistically significant for all the variables. Both the ammonia and chlorine dosage together explain 74.3% of the formation of chloramines, which is highly significant as indicated by the F-value (F=313.979).

Table 2: Modal summary

R	.862
R^2	.743
Adjusted R^2	.74
Std error of the estimate	.02578

It was also assumed from the normal probability plot of Figure 3 that the cumulative probability measured and observed values approach normal distribution, as all the points are lying near the straight line, which is the identical situation of normality. The model coefficients and their level of significance are shown in Table 3.

Table 3: Regression coefficients in the chloramines formation model

Variables	β	Standard errors	t-values	p
Constant	-.031	.009	-3.485	.001
Ammonia	.552	.034	16.015	.000
Chlorine dosage	.020	.003	6.077	.000

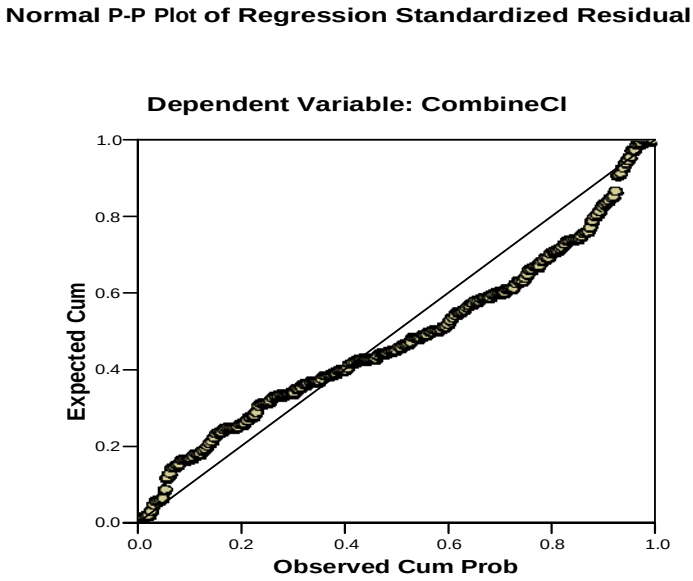

Fig.3: Normal probability plot of measured vs. predicted cumulative probability values for chloramines

Model validation

The final step of the chloramines formation model-bulding is the validation of the model. Validation of the fitted regression equation is the conformation that this model is effective and sound for the estimating the formation of the chloramines. Validation is a process involving a repeated of the experiment and the chloramines analysis to validate the equation in the initial study if similar results for the regression coefficients, predictive ability, and the like are obtained.

A means of measuring the actual predictive capability of the model is to use this model to predict each case in the new data set and then to calculate the mean of the square prediction error, to be denoted by MSPR [14], called mean squared prediction error:

$$MSPR = \frac{\Sigma_{i \to n} (Y_i - \Psi_i)^2}{n}$$

where:

Y_i is the value of the response variable in the i th validation set
Ψ_i is the predicted value for the i th validation case based on the model-building data set
n is the number of cases in the validation data set

A comparison between predicted and observed values for this model is presented in table 4. It can be observed that the model provides a satisfactory estimation of the concentrations of chloramines formation. The model is statistically significant and the value of the regression coefficients (r^2) was 0.343, which is a satisfactory level of explanation of the observed variability.

Table 4: Statistical evaluation of the chloramines formation model validation

Validation Parameters	Statistics
Number of validation data set	67
Degree of freedom	66
Average prediction bias	0.017462
% error of prediction	27.86 %
Variance of prediction error	0.018
Standard deviation	0.13319
Standard error of the estimated mean bias	0.01627
t-value (t critical)	-1.070 (2.000)
MSPR	0.035
MSPR error	1.6 %
Eta square	0.01705

Test was done on the model to determine the statistically significant difference in the experimental and predicted value of the model. t_{value} for the model was compared to the $t_{critical}$. If the $t_{value} < t_{critical}$, it can be concluded there is no significant difference between the predicted and the experimental data. Although t-test shows the significant difference between two set of data, it does not tell about the magnitude of the intervention's effect. So, the eta square was calculated to calculate the effective size statistic using the following formula:

$$\text{Eta Square} = \frac{t^2}{t^2 + n - 1}$$

The results from the statistical analysis showed that there was not a statistically significant difference between the experimental data (M = 0.0627, SD = 0.0384) and the expected data from the model (M = 0.0801, SD = 0.1414), with the t-value = -1.070 (> t-critical). The probability value was 0.288 (> 0.05), and it can be concluded there was not a significant difference between the expected and the real experimental data. The eta square value (0.02) can used to conclude there was small effect, with substantial difference between the two-set data.

Qualitatively, a visual inspection of a plot of measured values vs predicted values was presented in Figure 4 and can serve as a measure of model fitness. The model validation indicated reasonable prediction of chloramines formation. Based on the results of modeling and validation, it can be indicated that the chloramines formation was a function of chlorine dosage and the ammonia concentration in the raw water.

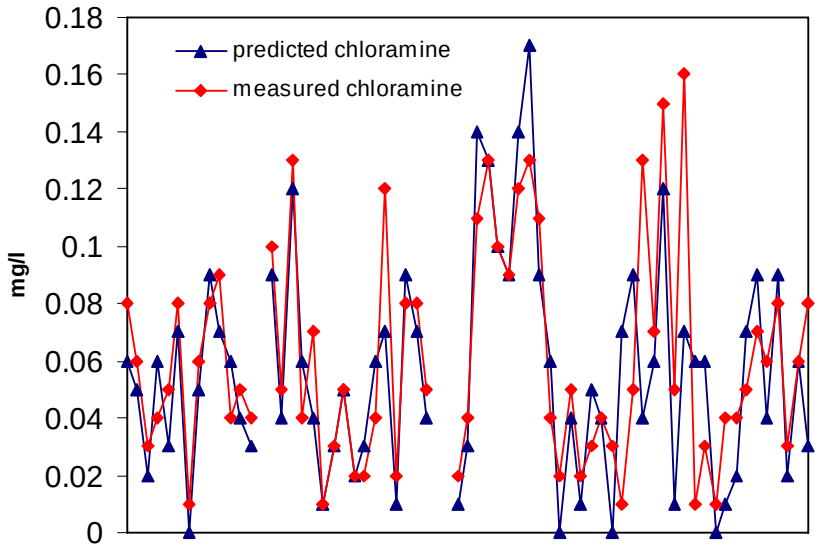

Fig. 2: Validation of the model for predicted and measured values of chloramines

Conclusions

This study was carried out to determine chloramines that result upon chlorination in Semenyih river water treatment plant. The dosing of chlorine to filtered water containing ammonia and organic nitrogen compounds may result in the formation of chloramines. Monochloramine was the dominant species detected in the treated water with 92 % in concentration of the total chloramines. Nitrogrn trichloride was the least proportion of chloramines observed in this study. This may due to the relatively constant pH and the unfavorable chlorine and ammonia ratio. The main purpose of this study was to develop statistically valid model from 220 experiments and 67 validation data. In order to predict the chloramines formed concentrations, correlation and regression analysis was conducted. A statistical significance ($p<0.05$) was utilized for the equation. The model was then validated and it was proven that it could provide a potential tool to predict the chloramines formation. The square root of MPSR gives 0.19 mg/l and the t-test result indicated that the regression equation is adequate for estimating the chloramines evolution using modeling approaches.

Acknowledgements

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