MODEL DEVELOPMENT FOR ASSESSING BULK CHLORINE DECAY RATE IN WATER FROM TREATED WATER SUPPLY IN KADUNA – NIGERIA

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ABSTRACT

Residual chlorine in water distribution systems is an important parameter needed for ensuring the standard of potable water supplies. This research investigates the bulk chlorine decay rate in water from public treated water supply from Kaduna North water treatment plant, Malali-Kaduna, Nigeria. The data generated from the study was used to validate a mathematical model of residual chlorine versus time developed using POLYMATH 6.10 professional software. The initial average residual chlorine value of 0.323 mg/l of the treated water obtained is lower than the recommended World Health Organization (WHO) value of 0.5 mg/l. The resultant model was found to be: $R_{ch} = 0.2808687 - 0.0030073t$. *Comparison of the results of the simulation of this model and the experimental data shows a good correlation with values of* R^2 *(a measure of the closeness of the data to the fitted regression line) and* R^2 *adj as 0.961 and 0.956 respectively. The model can therefore be used as an alternative to the manual method of determining the variation of residual chlorine along the treated water distribution network. The research revealed the need for booster chlorination after one hour along the distribution line or application of higher mass rate of chlorine at the source to maintain the minimum residual chlorine up to the farthest end.*

***Key words**: Chlorine, Decay Rate, Water Distribution System, Modeling, Simulation*

1. INTRODUCTION

According to American Water Works Association (AWWA), 2004, the earliest recorded use of chlorine directly for water disinfection was on an experimental basis in connection with filtration at Louisville, KY in 1896. The advantages of chlorine disinfection include simplicity, low cost and a broad range of effectiveness such as controlling aesthetic quality, removing iron, manganese, and hydrogen sulphide; sterilizing mains and storage tanks; restoring and preserving pipeline capacity and maintaining distribution system bacterial quality by reducing the growth of microorganism and slimes (Abdullahi and Abdulkarim, 2010; Hua *et al*., 1999; Vasconcelos *et al*., 1997).

When chlorine is dissolved in water, it hydrolyzes to form hypochlorous and hydrochloric acid as follows;

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad (1)$$

The hypochlorous acid further ionizes or dissociates into hydrogen and hypochlorite ions as follows;

$$HOCl \leftrightarrow H^+ + OCl^- \qquad (2)$$

The oxidizing effect on micro-organisms is produced by both hypochloric acid and hypochlorite ions (Eryilmaz and Palabiyik, 2013). When Chlorine is used for disinfection, it reacts readily with oxidizable substances such as Fe^{2+} and Mn^{2+} and other organic matters. Thereafter, chlorine reacts with ammonia to form chloramines (monochloramine, NH_2Cl and dichloramine, $NHCl_2$) which further oxidize with more chlorine to trichloramine NCl_3 (Nitrogen trichloride). Research results have also revealed that chlorine decay occurs due to reactions with materials associated with the pipe wall resulting in corrosion and biomass growth on the inner pipe walls (Kowalska *et al*., 2006). The break point is reached when these reactions are completed so that continued addition of chlorine produces free residual chlorine (White, 1986). Therefore, residual chlorine can be defined as the concentration of all oxidizing agents produced by chlorination of natural water that remains after a certain period of time. Its measurement is done to determine the efficiency of disinfection.

Chlorine dosages in distribution systems are determined primarily by the need to ensure minimum chlorine residual in the distribution system water so as to eliminate disease causing microorganisms or substances that adversely affect the taste and quality of the distributed water as well as the condition of the distribution system. On the other hand, control of excess chlorine doses is required to reduce the extent of formation of disinfection byproducts (DBPs) that are known for causing health related risks in humans (Tiruneh *et al*., 2016). Rossman *et al*. (2001) define the bulk chlorine decay as chlorine reaction with dissolved and suspended matter, mostly natural organic matter (NOM) in the water, thus the chlorine reactions with compounds attached to or derived from pipe materials can be ignored. In most waters, the reactions of chlorine with NOM make up the majority of the chlorine demand. Bulk decay may be isolated from wall decay by carrying out chlorine decay experiments on the source water under controlled conditions in laboratory (Hua *et al*., 1999)

A water distribution system (WDS) is a hydraulic conveyance system laid on road shoulders where topology and topography are known and that transmit water from the source to the consumers. It consists of elements such as pipes, valves, pumps, tanks and reservoirs, flow regulating and control devices (Bello *et al*., 2015). According to Vasconcelos *et al*. (1997), proper understanding, characterization, and prediction of water quality behavior in the water distribution systems are critical to meeting regulatory requirement and consumer-oriented expectations. This can be achieved through computer-based modeling and simulation of the water quality variables along the distribution systems with time.

A model is a simplified representation of a system intended to enhance our ability to understand, explain change, preserve, predict and possibly control the behaviour of a system. Modeling is thus the process of establishing inter-relationship between important entities of a system (Abdulkareem, 2000); while simulation is a means of gaining relevant information on the characteristics of full size prototypes without incurring the expenses of building a full size prototype to test (Morley, 1979). According to Kowalska *et al*. (2006), it is difficult to predict chlorine decay in large distribution systems, especially if they work under poor hydraulic conditions (aged pipes, small velocities, etc.). Therefore, when testing chlorine decay, it seems easier to separate the reactions associated with the bulk liquid from those associated with the pipe wall. Mathematical modeling of chlorine decay in distribution systems is essential in order to be able to predict chlorine residuals with reasonable accuracy and reduce the cost and time associated with monitoring. In large distribution systems, monitoring of chlorine residuals may be prohibitively expensive (Tiruneh *et al*., 2016). Therefore, computer based model will be a promising cost effective alternative (Vasconcelos *et al*., 1997).

In recognition of the importance of residual chlorine as an essential final check to the quality of water supply to the consumer, a number of researches have been conducted on chlorine decay kinetics and development of model to predict chlorine decay in drinking water in recent time (Castro and Neves, 2003; Georgescu and Georgescu, 2012; Goyal and Patel, 2014; Hua *et al*., 1999; Kowalska *et al*., 2006; Tiruneh *et al*., 2016; Vasconcelos *et al*., 1997). However, there is still need for further research in this area particularly in developing countries like Nigeria, where water distribution system is characterized with over dependence due to excessive growth in population and intermittent supply of water. To cope with high demand, the service areas are usually divided into few zones and each zone receives supply for limited hours which leads to the stagnation of water in pipes during non-supply hours and decay of chlorine for rest of the hours. The intermittent supply scenario exposes consumers to health risks due to the higher likelihood of contamination of water pipelines through joints and damaged segments during periods when the system is not pressurized. Also, there is a problem related to maintenance of pressure at the farthest node in intermittent water supply.

According to Kowalska *et al.* (2006), the residence time of water in any distribution system changes the quality of the water, because the values of many parameters decrease or increase as a result of chemical and biological reactions which depend on the environment in the distribution system. This research investigates the variation of residual chlorine with time in water from public treated water supply from Kaduna North water treatment plant, Malali-Kaduna, Nigeria and to use the data generated to develop a mathematical model relating residual chlorine with time using polymath software. This study is significant because the effect of residence time on concentration of residual chlorine is a necessary check for both the chlorine application strategy which guides the selection of supply hours of water to achieve the effectiveness of booster chlorination strategy for the intermittent water supply.

2. MATERIALS AND METHODS

Study Site and Sample Collection

The study area is the Kaduna North water treatment plant, Malali-Kaduna, Nigeria. The treated water samples were collected using sample bottles sterilized with sulphuric acid and washed thoroughly with distilled water. The samples were taken at the point of discharge to consumers at the water treatment plant once weekly for a period of three weeks.

Determination of Residual Chlorine

The residual chlorine was determined using a NN Diethyl-Pthenogene Diamine reagent (DPD test). The test was carried out in a British Drig House (BDH) comparator which comprises of two 10 ml cuvettes, two standard discs, 3/40/A and 3/40/B disc with range of residual chlorine measurements of 0.1 – 1.00 and 0.2 – 0.4 mg/l respectively. The first tests were carried out at the point of collection to avoid any time lapse, while the subsequent tests where carried in the laboratory.

For each batch of test, a cuvette was filled with 10ml of the sample and inserted into the left compartment of the BDH comparator. The second cuvette was then filled to about 2cm of its depth with the same sample and a DPT tablet was then dropped into it and allowed to dissolve completely. The mixture was then inserted into the right compartment of the comparator and then observed. A pink colour development indicates the presence of residual chlorine. The value of the residual chlorine was determined by rotating one of the discs until a colour march is attained in the viewing window and the residual chlorine was directly read through the window in the lower right hand corner of the comparator. This was repeated for all the samples at intervals until no residual chlorine was observed.

Modeling Procedure and Statistical Analysis

A simple linear regression model for an outcome y as a function of a predictor x takes the form:

$$y_i = \beta_0 + \beta_1 x_i + c_i \qquad (3)$$

for i = 1, ………, n

Where n represents the number of observations (rows) in the data set (Model Data Science with R, 2017).

Kowalska *et al*. (2006) states that the water quality parameter changes with the residence time of water in any distribution system. A study by Franson (1994) shows that chlorine demand for water disinfection is dependent on the time of contact. The relationship between the residual chlorine and time can be expressed mathematically as (Abdullahi and Abdulkarim, 2010):

$$R_{cl} = f(t) \qquad (4)$$

Introducing a constant, Equation (4) becomes:

$$R_{cl} = a_1 t \qquad (5)$$

To correct variations from other factors such as temperature, pH etc. (Zheng, 2013) not accounted for, a constant a_0 is introduced, thus Equation (5) becomes:

$$R_{cl} = a_0 + a_1 t \qquad (6)$$

Where: R_{cl} = Residual Chlorine

a_0 and a_1 are constants

t = time

Using POLYMATH 6.10 professional software, the values of these constants can be evaluated and substituted into Equation (6) to obtain the model equation.

The statistical analysis and the linear fit of plot of predicted versus actual experimental residual chlorine values was obtained using OriginPro 8.0 software.

3. RESULTS AND DISCUSSION

Effect of residence time on Chlorine concentration in treated water samples

The values of residual chlorine determined from the treated water samples with respect to time once per week for a period of three weeks and the average values are presented in Table 1. An initial average observed value of 0.323 mg/l can be considered inadequate because according to WHO (1993), a residual concentration of free chlorine of greater than or equal to 0.5 mg/L (0.5 ppm or parts per million) after at least 30 minutes contact time at pH less than 8.0 is recommended for treated water (CDC, 2014). However, this will only be appropriate when users drink water directly from the flowing tap. It has been found that while a residual chlorine level of 0.5 mg/L at the treatment plant may be enough to maintain the quality of water throughout the distribution network; however, it is most likely not to be adequate to maintain the quality of the water at this residual chlorine level when the water is stored at home in a bucket or jerry can for over 24 hours. The United States Centre for Disease Control and Prevention therefore recommends initial residual chlorine of 2.0 mg/L at the point of dosage.

Table 1: Experimental values of Residual Chlorine

S/No.	Time (Min)	Residual Chlorine (mg/l)			
		Week 1	Week 2	Week 3	Average
1	0	0.3	0.32	0.35	0.323
2	5	0.25	0.28	0.27	0.267
3	23	0.2	0.21	0.22	0.21
4	30	0.15	0.16	0.15	0.153
5	45	0.125	0.13	0.125	0.127
6	55	0.1	0.1	0.1	0.1
7	70	0.07	0.08	0.07	0.073
8	80	0.03	0.03	0.04	0.043
9	95	0	0	0	0
10	100	0	0	0	0

Figure 1 shows a gradual decrease in average residual chlorine values from 0.323 mg/l at 0 minute to 0 mg/l after a residence time of 95 minutes. This is as a result of further reactions of chlorine with dissolved and suspended matter which are usually natural organic matter (NOM) in the water along the distribution line. This is in accordance with the findings of Kowalska *et al*. (2006) which states that the water quality parameter changes with the residence time of water in any distribution system. This decrease in chlorine concentration with time is referred to as chlorine decay (Goyal and Patel, 2014). The result also shows the need for booster chlorination along the distribution network after every 60 minutes residence time of treated water in the supply pipeline. The booster chlorination helps in maintaining proper balance between the minimum and maximum residual chlorine concentrations. Alternatively, to cope up with the decay in chlorine, higher mass rate of chlorine is applied at the source to maintain the minimum residual chlorine up to the farthest end, however, studies have also shown that this may result in harmful disinfection by-products (DBP) formation at the nearest locations to the source and less concentration of residual chlorine at farthest location (Goyal and Patel, 2014).

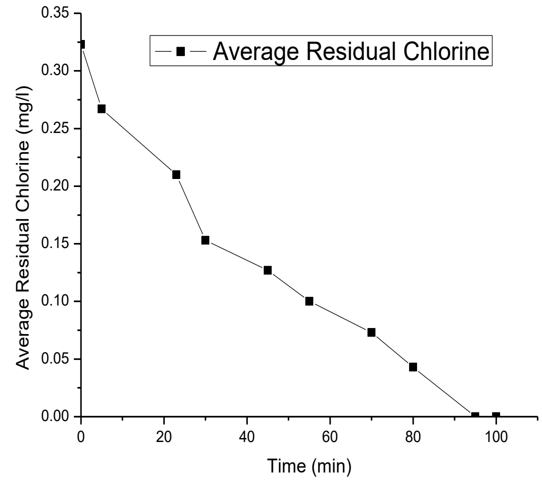

Figure 1: A plot of Average Residual Chlorine (mg/l) against time (min)

Modeling and Statistical Analysis

The model of the relationship between the average chlorine value and time was determined by substituting the experimental average residual chlorine values into the POLYMATH 6.10 professional software. The resultant model was found to be:

$$R_{ch} = 0.2808687 - 0.0030073t \qquad (7)$$

The result of the simulation of the model (Equation 7) is shown in Table 2.

Table 2: Simulated Values of Residual Chlorine

S/No.	Time (Min)	Residual Chlorine (mg/l)
1	0	0.2809
2	5	0.2658
3	23	0.2117
4	30	0.1906
5	45	0.1455
6	55	0.1155
7	70	0.0704
8	80	0.0403
9	95	-0.0048
10	100	-0.0199

A plot of simulated residual chlorine values against time (Figure 2) gave a straight line which shows a regular decrease in the simulated residual chlorine values (ideal situation) with negative residual chlorine values of -0.0048 and -0.0199 at 95 and 100 minutes respectively which are not obtainable in real situations. This may be attributed to the effect of other factors such as pH and temperature not taking into consideration during the development of the model (Zheng, 2013).

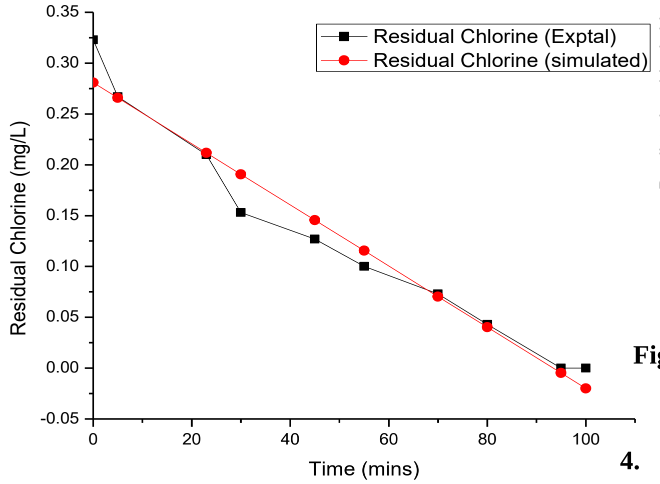

Figure 2: A plot of experimental and simulated residual chlorine values against time

Statistical analysis of the result using OriginPro 8.0 software gave the values of the correlation coefficient (R^2) and adjusted R^2 as 0.961 and 0.956 respectively. *R-squared* is a statistical measure of how close the data are to the fitted regression line. It is also known as the coefficient of determination, or the coefficient of multiple determinations for multiple regressions. The R^2 coefficient gives the proportion of the total variation in the response predicted by the model, indicating ratio of sum of squares due to regression (SSR) to total sum of squares (TSS). The R^2 value was found to be closed to adjusted R^2 value of 0.961 showing a good relationship between simulated and experimental values. A high R^2 value, close to 1, is desirable and a reasonable agreement with adjusted R^2 is necessary (Ghafari *et al.*, 2009). A high R^2 coefficient ensures a satisfactory adjustment of the model to the experimental data.

The linear fit of plot of predicted versus actual experimental residual chlorine values (Figure 3) shows a straight line with an error of 0.0408. This indicates good prediction of experimental data using the model. Actual values are the measured values for a particular experiment, whereas predicted values are generated by using the approximating functions.

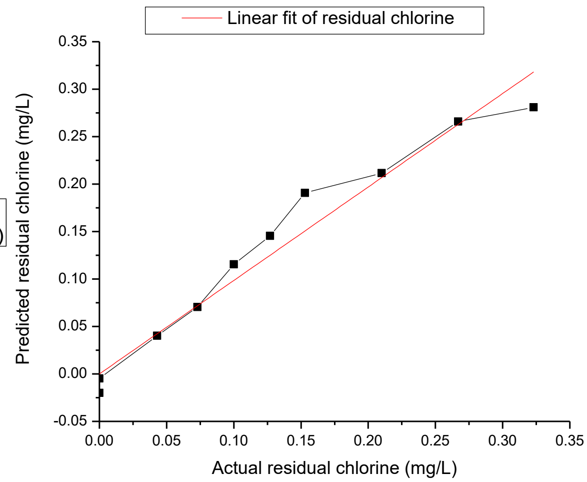

Figure 3: A plot of predicted versus actual experimental residual chlorine values

4. CONCLUSION

The objective of this research was to assess the bulk chlorine decay of treated water samples from Kaduna North water treatment plant, Malali-Kaduna, Nigeria under controlled conditions in laboratory and to use the results obtained to validate a model of the change in residual chlorine versus time developed using POLYMATH 6.10 professional software. The major conclusions drawn from the results are:

1. The initial average residual chlorine value of 0.323 mg/l of the treated water is lower than the recommended WHO value of 0.5 mg/l.
2. The result revealed the sensitivity of residence time to residual chlorine hence the need for booster chlorination after one hour (1 hr) along the distribution line or application of higher mass rate of chlorine (0.5 mg/l) at the source to maintain the minimum residual chlorine up to the farthest end.
3. The resultant model gave a good prediction with values of R^2 and R^2 adj as 0.961 and 0.956 respectively. The model can therefore be used as an alternative to the manual method of determining the variation of residual chlorine along the treated water distribution network.

5. RECOMENDATION

Further researches should focus on the effect of reactions with materials associated with the pipe wall resulting in corrosion and biomass growth on the inner pipe walls on residual chlorine.

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