Effects of water quality characters on chlorine decay in water distribution networks

Theses of the PhD Dissertation

by

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Budapest, 2017

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Introduction

1.1. Background

Depending on the quality of water, types of treatment processes and the condition of distribution system, behavior of chlorine decay behavior is significantly variable. Further, application of chlorination and the presence of chlorine residuals lead to form the disinfection by-products (DBPs) in the treated water (USEA, 2006). These by-products result due to chlorine reactions with the natural organic matter contained in water. Due to its harmful effects on the human health, more concentration has been paid on the formation of these by-products over the last years (Hrudey, 2009; King et al., 2000).

In Hungary, most significant quality problems of drinking water resources are the ammonium, iron, manganese and arsenic content. Generally, there are two technologies are applied in most of Hungarian water utilities, to remove ammonium from the raw water, which are the breakpoint chlorination and biological ammonium removal. Some studies showed that applying the breakpoint chlorination enhances the formation of disinfection by-products (DBPs) such as the adsorbable organic halogen (AOX) and trihalomethane (THM) in water distribution system. Therefore, the focus on the biological treatment as alternative technology to eliminate ammonium was increased without consideration their effect on the chlorine decay and by-products (DBPs) formation.

Accurate prediction of chlorine decay through water systems becomes crucial to our water management. Many different models have been proposed and evaluated for modeling chlorine decay. (Shang et al., 2008). These models are typically based on many water quality parameters (Chowdhury et al., 2009).

1.2 Objectives of the research

This work aims to investigate the influence of biological ammonium removal technology on the kinetics of chlorine decay and disinfection by-products (DBPs) formation in operated water treatment plant. In addition to investigate the effects of pre-UV disinfection, initial chlorine concentration and natural organic matter (NOM) on the behavior of the chlorine decay.

On 2011, the studied water supply system had applied a replacement process for the network pipes in parallel with applying different treatment technology in the water treatment plant (the biological ammonium removal). During the initial investigation, it was observed high decay for the residual chlorine in the water supply network.

Due to these observations, series of experiments on different water samples have been carried out to determine the reasons that lead to this fast decay for the chlorine.

On the other hand, this research aims to evaluate and compare different kinetic chlorine decay models in terms of their potential to properly predict the chlorine residual in bulk water. As well it aims to develop a mathematical equations for modeling the chlorine decay coefficients as function of initial chlorine concentrations and organic matter.

2. Initial water quality analyzing

Since November 2011, new treatment technology started operating in order to improve the water quality and to achieve effective removal for ammonium. The new treatment consists of aeration the extracted raw water from the wells (there is no raw water storage tank), followed by fluidized bed filtration (biological ammonium removal), disinfection by UV-irradiation, rapid sand filtration, disinfection by chlorine gas, two water storage tanks and a cartridge filter.
Chemical, physical and microbiological data of water quality which collected at different locations by the water utility have been analyzed. These data were collected over ten years from 2003 to 2013.

The data evaluation showed significant decreasing in ammonium concentrations about 99 % after the biological removal. As well, iron and manganese concentrations had reduced about 96% and 94% respectively in the treated water.
On the other hand, gradual increase in THM concentrations was observed in the pipe network after the starting with these new treatment process (Fig. 1).

3. Investigation of factors affect the bulk chlorine decay

Three types of water samples were collected from the water treatment plant (DWTP):

- raw water samples (RW),
- samples from the effluent of the Bio-fitters before UV disinfection (BUW),
- Finally, samples from the effluent of DWTP before chlorination (TW).

To study the effect of biological ammonium removal technology on chlorine decay, raw water samples (RW) were treated by natural zeolite filtration (FW), and then chlorinated with different initial chlorine concentrations and compared with a series of TW samples which were chlorinated with the same doses. It was found that the bulk chlorine degradation in the filtered sample (FW) was around the same in the bio-filtered one.

The influence of pre- UV disinfection on bulk chlorine decay was also studied; series of chlorine decay experiments were performed on water samples collected before and after UV irradiation unit. No considerable difference was observed in the chlorine decay curves between UV treated (TW) and non UV–treated (BUW) samples. In both

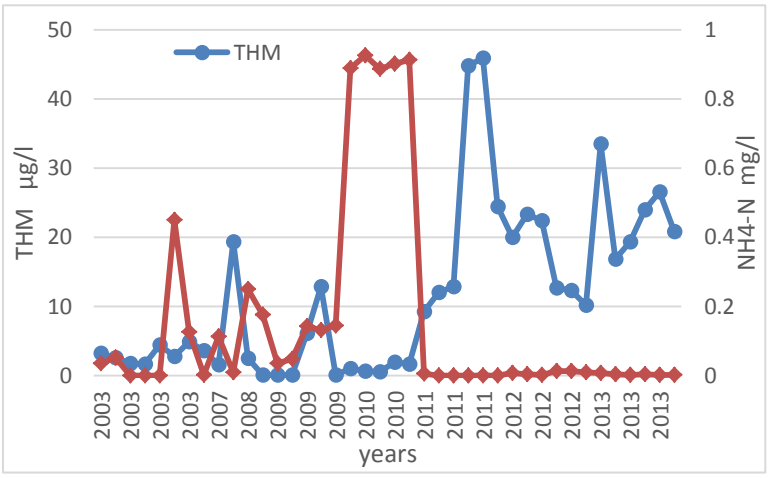

Fig. 1: THM and ammonium concentrations in the studied water distribution network

samples, chlorine consumption through the first 1 hour was about 66% and 72% for initial chlorine doses 1.5 and 1.1 mg/L respectively.

TW samples were dosed by various chlorine doses ranged between 1.2 to 3.0 mg/L to investigate the effect of the initial chlorine concentration on the kinetic of chlorine decay. It was found that in all cases, chlorine decay decreased by increasing the initial chlorine concentration

On the other hand, to study the effect of the natural organic matter (NOM) on bulk chlorine decay, powdered activated carbon (PAC), granular activated carbon (GAC), coagulation and dilution process have been applied on TW water in order to reduce and vary the organic content in treated water samples. After that, the chemical oxygen demand (COD_{Mn}) for each sample was measured to investigate the efficiency of the organic matter removal.

Further, all samples after each organic matter removal treatment were chlorinated and the residual chlorine concentrations were measured.

The efficiency of PAC and GAC in removing organic matter was similar, and the remaining COD_{Mn} concentrations were about 0.48 and 0.56 mg/L in all samples after adsorption by PAC and GAC respectively.

The result of studying the influence of organic materials on bulk chlorine decay showed decreasing in the chlorine demand by reducing COD_{Mn} concentrations.

As well, varying the organic content in the water samples has affected significantly on the chlorine degradation. Reducing COD_{Mn} concentrations from 1.44 to 0.8 mg/L led to increase the residual chlorine concentration from 0.6 to 1.0 mg/L for the same contact time (28 h) and the same initial chlorine concentration (1.5 mg/L).

4. Modeling of chlorine decay

To investigate the kinetics of bulk chlorine decay, two sets of experimental data have been used:

1- The first set was obtained by chlorination the effluent samples (TW) of the water treatment plant (samples were collected after treatment, but before final chlorination) which have COD_{Mn} concentration about 2.0 mg/L with six initial chlorine concentrations: 1.2, 1.5, 1.8, 2.0, 2.5 and 3.0 mg/L.
2- The second experimental data set was defined to investigate the effect of the organic content by dosing each diluted sample which has different COD_{Mn} concentrations (0.8, 0.96, 1.2, 1.44, 1.6, 2.0 mg/L) with two initial chlorine concentrations: 1.2, 1.5 mg/L.

Firstly, the first set of experimental data was used for evaluation the single-constituent decay models (Table.1). The coefficients of each bulk chlorine decay model were estimated by using the least square method by setting up the Solver function in Excel to minimize the sum of the squared errors between predicted and observed values of chlorine concentrations.

Table.1: Bulk chlorine decay models in water distribution system

Kinetic Model	**The differential form**	**the integrated form**	**coefficients**
n^{th} order model	$dC/dt = -k C^{n}$	$C_{(t)} = (kt (n-1) + (1/C_o)^{(n-1)})^{(-1/(n-1))}$	k , n
limited first order model	$dC/dt = -k (C - C^*)$	$C_{(t)} = C^* + (C_o - C^*) \exp(-k t)$	k , C^*
parallel first order model	$dC/dt = -k_1 C_1 - k_2 C_2$	$C_{(t)} = C_o x \exp(-k_1 t) + C_o(1-x)\exp(-k_2 t)$	k_1, k_2 , x
second - order model	$(dC_A)/dt = -k_A C_A C_B$ $(dC_B)/dt = -k_B C_A C_B$	$C(t) = [C_{A,o} (1-K)] / [1-K e^{(-ut)}]$ $u = M(1-K)$, $K = a C_{B,O} / b C_{A,O}$	K , M

Comparison of the single-constituent decay models showed that the parallel first - order model provided the best fit between the measured and predicted data, with correlation coefficients (R^2) ranged between 0.95 - 0.99 (Fig.2).

Afterwards, the second experimental data set has been used for additional investigations of the parallel first - order model. MATLAB software was used to estimate the coefficients of the parallel first-order model by application, called Curve Fitting (cftool), which provides the model parameters via the nonlinear least squares method.

It was found, that the parallel first- order model represents an accurate prediction of chlorine residual for all data series which have different COD_{Mn} concentrations.

On the other hand, two - constituent decay model (second - order mode, Clark 1998). was applied on the both sets of experimental data (Table.1). The model coefficients (*K*, *M*) were estimated by using MATLAB's application (cftoot).

The second-order model appeared to have good capacity in prediction the residual chlorine. It was noticed from the first estimation of the model coefficients, that the estimated coefficients (*K*, *M*) are not independent from the chlorine dose and organic content (Fig.3).

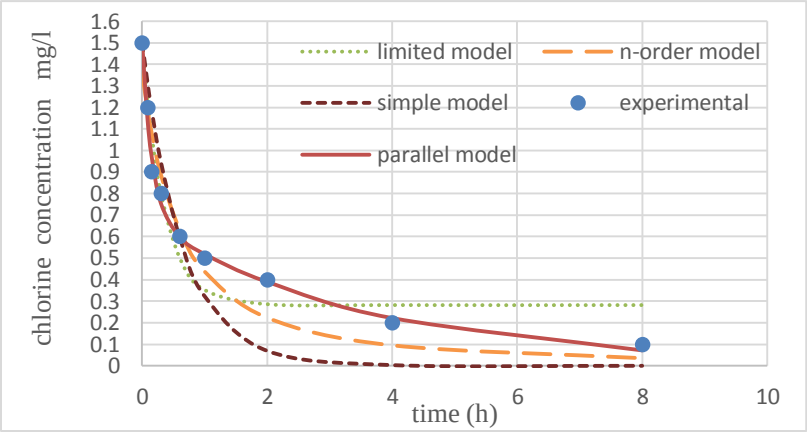

Fig.2 . Comparisons of single-constituent chlorine decay models for Co=1.5 mg/L

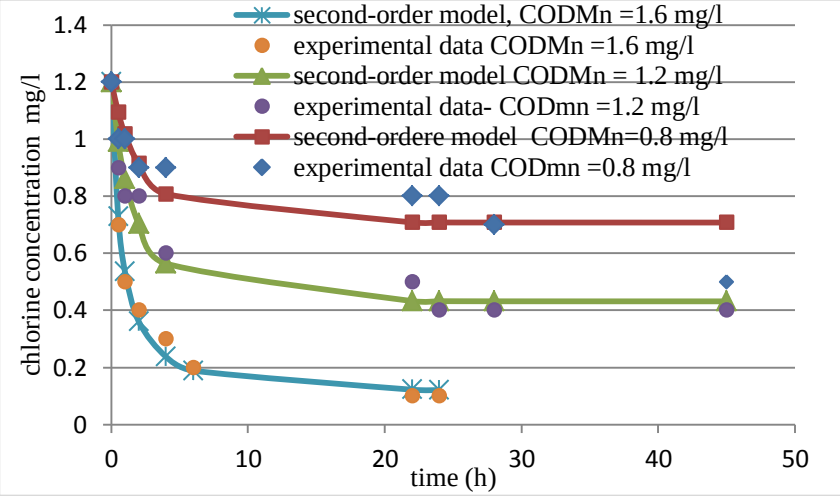

Fig.3 . Bulk chlorine decay according to the second - order model in case three different COD_{Mn} concentrations (0.8 mg/l; 1.2 mg/l; 1.6 mg/l)

4.1. Modeling the combined effect of initial chlorine concentration (Co) and COD_{Mn} on the models coefficients

The coefficients of the selected models (parallel first and second - order model) had been evaluated and developed by relating them with different water quality parameters.

- *The parallel first order*

During the first estimation for the parallel first order coefficients, it was found that they were varying with initial chlorine (C_o) and COD_{Mn} concentrations. In order to describe

the behavior of these coefficients as functions of the control variables (C_o, COD_{Mn}), graphical approach has been used. Each coefficient (k_1, k_2, x), was plotted against each control variable in turn, while holding the other control variables roughly constant.
It was found that the determination coefficients (R^2) for both the rapid (k_2) and slow decay (k_1) coefficients were about 0.89, which shows a strong relationship between these variables. On other hand, it was observed a clear increasing in the values of the fraction of chlorine, which reacts slowly (x), by increasing the initial chlorine concentration (C_o).
The influence of organic matter on parallel first – order model coefficients was also studied. It was observed that k_1, k_2 values have proportionally increased by increasing COD_{Mn} concentrations. Concerning x, an inverse relationship was found between this coefficient and COD_{Mn} concentrations.

Depending on the previous correlations, empirical equations had been derived and developed to account for the combined effects of the initial chlorine concentration (Co) and COD_{Mn} on the coefficients k_1, k_2 and x.
The equations constants have been estimated by transforming these equations into natural logarithms, then running Multiple Regression Analysis. The yielded equations were:

$$k_1 = 0.00057\ {C_o}^{-3.2}\ e^{3.42\ COD} \quad (1)$$

$$k_2 = 1.53\ {C_o}^{-1.02}\ e^{0.44\ COD} \quad (2)$$

$$x = 0.52\ {C_o}^{0.71}\ COD^{-063} \quad (3)$$

Independent data have been selected randomly to verification the empirical equation. The results showed good correlation between the predicted and measured data.

- *The second - order model*

In similar way, the influence of initial chlorine concentration (C_o) and COD_{Mn} on the second - order model coefficients was investigated by plotting the estimated values of each coefficient (K, M) against C_o and COD_{Mn} concentrations separately.

Inverse correlation between K, M and the initial chlorine concentration (C_o) was observed, while the relationship between COD_{Mn} and each coefficient (K and M) was proportional. Therefore, it can be seen that K and M values increased by increasing COD_{Mn} concentrations in water samples.

Two empirical relationships between C_o, COD_{Mn} and the second order model coefficients (K, M) have been derived and compared. To evaluate the constants of empirical relationships, multivariate regression analysis was applied. Again, MATLAB

software was used to estimate the constants of each functional relationship by non-linear regression. The yielded equations were:

$$K = 0.58\ C_o^{-0.26}\ COD^{0.76} \quad , \quad M = 1.29\ C_o^{-2.33}\ COD^{1.26} \qquad (4)$$

$$K = 0.41\ e^{(-0.17*Co)}\ COD^{0.5} \quad , \quad M = 9.8\ C_o^{-3.13}\ e^{(1.2*COD)} \qquad (5)$$

Performance of each empirical equation was investigated by applying them on independent data. Although the differences between the both examined empirical equations was slight, it was suggested that the represented function in Eq. 4 is significantly better for describing the correlation between the coefficients of second-order model (*K, M*) and each water quality parameter (Co and COD_{Mn}), (Figs 4 and 5).

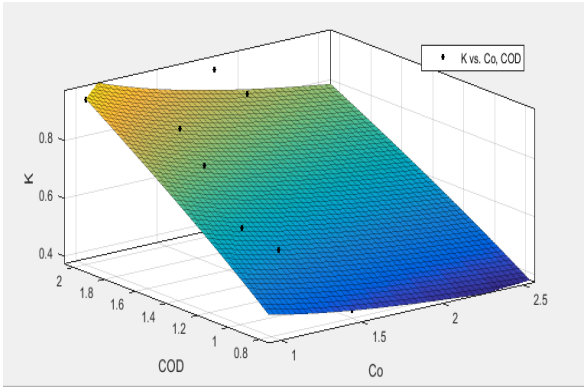

Fig 4: The functional relationship between COD_{Mn} , Co and K

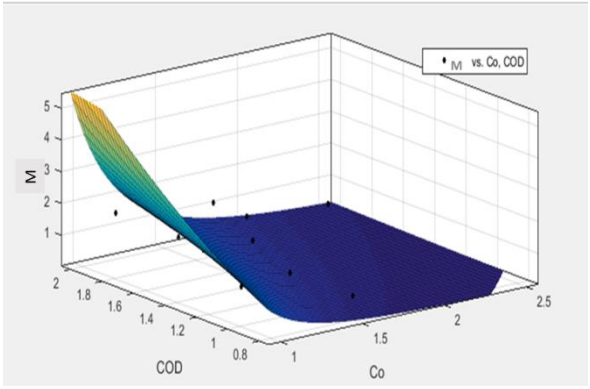

Fig 5: The functional relationship between COD_{Mn}, Co and M

4.2 Validation of bulk chlorine decay models

In order to test the ability of both parallel first – orders model and second - order model to predict the bulk chlorine concentrations, the yielded empirical equations (Eq .1. 2 . 3 and 4) of each model coefficients have been used to calculate the parameters of the integrated form of the parallel first and second - order models, Eq.6 and Eq.7 respectively. 124 of experiments data were selected randomly and did not use for the model development was used for validation the models.

$$C(t) = C_o\, x\; e^{(-k_1\, t)} + \; C_o\, (1 - x)\, e^{(-k_2\, t)} \quad (6)$$

$$C_A(t) = \frac{C_{A,o}\,(1-K)}{1-K\; e^{(-ut)}} \quad (7)$$

Where:
$u = M\,(1 - K)$

The results showed slight differences between parallel first- and second- order models in describing the behavior of the chlorine decay. However, the second-order has been suggested because it gave better fitting between the predicted and the observed bulk chlorine concentrations.

To maintain residual free chlorine in water distribution networks, and to reduce the by - products (DBPs) formation in the water treatment plant (WTP) which are using the biological ammonium removal, it is necessary to provide an organic matter removal in the water treatment plant, such as granular activated carbon adsorption (GAC), or any other possible treatment before the chlorination.

5. New scientific theses

Thesis.1: biological ammonia removal

By this research, it was found that applying chlorination after the biological ammonia removal enhances by-products formation, especially THM formation. During the work, it was observed gradual increasing in THM concentrations in the studied water network since starting with the biological ammonium removal treatment in the studied water treatment plant. Limited researches had studied the correlation between the biological ammonium removal and THM formation. Here in this work, we found that even of the advantages of biological ammonium removal in decreasing the inorganic compounds and other materials, there is still drawback for this technology concerning the THM appearance. This result has been confirmed with some results from other waterworks concerning the THM formation after applying the biological ammonium removal in the water distribution system

Thesis.2: organic matter

The effect of the natural organic matter (NOM) on bulk chlorine decay was experimentally investigated by applying powdered and granular activated carbon (PAC, GAC) adsorption, as well, by dilution the water samples with distillated water to change the organic matter concentrations in treated water samples (TW).

The results showed that the organic content has the most significant influence on the bulk chlorine decay and by-products DBPs formation, where iron, manganese and ammonia concentrations were less than the allowable limit in the finished treated water according to the current Hungarian regulation (Government Decree No. 201/2001).
Proportional correlation between the bulk chlorine decay rate of treated water and its organic content was observed. The bulk chlorine decay rate in the water samples decreased by decreasing the organic matter concentration.

Thesis.3: simple methodology for modeling the bulk chlorine decay

In this work simple methodology was adopted, by considering COD_{Mn} concentration as control variable during modeling of bulk chlorine decay. This methodology could be appropriate for most of water utilities, where the possibility of total organic carbon (TOC) measurement is not available, and they depend on the permanganate index (COD_{Mn}) as organic matter indicator of the water.

Thesis 4: developing mathematical models of the coefficients

Two different kinetic models, the parallel first - and the second - order model were applied on the experimental data to simulate the bulk chlorine decay. It was found that the decay coefficients of both models significantly varied with the initial chlorine concentration (C_o) and organic content (COD_{Mn}) of water. Therefore, empirical equations had been derived and developed to account for the combined effects of these two parameters with the coefficients of each model.

The parallel first - order model and second - order model showed good correlation between the measured and predicted data after taking into consideration the effect of the initial chlorine concentration and the organic matter. The second-order model showed to perform better ($R^2 = 0.83$) than the parallel first - order model ($R^2 = 0.79$).

Thesis 5: dependency of the second order model coefficient (M) on the initial chlorine concentration

In this work, it was found that the coefficient of the second order model (*M*) was dependent on the initial chlorine concentration (C_o), where the correlation coefficient was about 0.81 and significant at 10% level. *M* values decreased by increasing the concentrations of the initial chlorine. Therefore, the coefficient of second order model (*M*) was determined and modeled as function of both COD_{Mn} and initial chlorine concentration (C_o).

6. Publication list:

- ***Thesis 1:***

Alheboos S., Licsko I . Effects of the water quality on chlorine decay in water distribution networks. 15th International Multidisciplinary Scientific Geo Conference SGEM 2015, Conference Proceedings, ISBN 978-619-7105-40-7 / ISSN 1314-2704, Book (5) Vol. (2), PP: 181-188. 2015
DOI: 10.5593/SGEM2015/B52/S20.024

- ***Thesis 2:***

Al Heboos Sonia, Dr. Licskó István. Influence of Water Quality Characters on Kinetics of Chlorine Bulk Decay in Water Distribution Systems. International Journal of Applied Science and Technology. Vol.(5), No.(4); PP : 64-73 . 2015

- ***Thesis 3:***

Sonia Al Heboos, István Licskó. Application and Comparison of Two Chlorine Decay Models for Predicting Bulk Chlorine Residuals. Period. Polytech. Civil Eng., Vol.(61), No. (1) (2017), pp. 7-13.
DOI: 10.3311/PPci.9273

- ***Thesis 4***

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DOI: 10.3311/PPci.9273

- ***Thesis 5***

S. Al Heboos. Investigation and modeling of bulk chlorine d decay kinetic in water distribution system . Proceedings of the IWA - 8th Eastern European Young Water Professionals Conference. pp : 344 – 350. 2016

Sonia Al Heboos, István Licskó. Application and Comparison of Two Chlorine Decay Models for Predicting Bulk Chlorine Residuals. Period. Polytech. Civil Eng., Vol.(61), No. (1) (2017), pp. 7-13. DOI: 10.3311/PPci.9273

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