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

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by
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Abstract

Several water quality parameters are contributing to the chlorine degradation in drinking water supply system. Water utilities are required to maintain minimum chlorine residuals throughout distribution systems for disinfection. However, maintaining this residual is a complicated task due to chlorine reaction with a wide range of organic and inorganic substances in water and formation of chlorine by-products, which are in some cases carcinogenic and harmful to human health.

These challenges highlights the importance of having an appropriate models for chlorine decay in bulk water as a pre-required step to model the chlorine decay in the distribution system.

The aims of this research are investigation the influence of the biological ammonium removal, initial chlorine concentration, pre - disinfection by ultraviolet irradiation (UV) and the organic content on the rates of chlorine decay. As well, characterizing the kinetics of chlorine decay in the treated drinking water, by applying several kinetics models.

The water samples were chlorinated under various conditions and chlorine levels were monitored as the reactions proceeded. As well as various treatments including zeolite filtration, coagulation, powdered (PAC) and granular activated carbon (GAC) adsorption, were applied on different types of water samples before chlorination. The observations of dissolved oxygen concentration, pH, iron, manganese, ammonium, trihalomethane (THM) concentrations in the water samples were reported.
In this work, single-constituent and two-constituent decay models have been investigated and evaluated for chlorine decay prediction especially in bulk water.

These models are based on data collected by the author. The coefficients of the kinetic models were defined as functions of initial chlorine concentration (Co) and COD_{Mn} (Chemical Oxygen Demand measured by potassium permanganate consumption) by developing mathematical equations relating these parameters.
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**Notation**

\( NOM \) natural organic matter

\( C(t) \) the chlorine concentration at any time \( t \) (mg/L);

\( C_o \) the initial chlorine concentration (mg/L);

\( C(t) \) the chlorine concentration at any time \( t \) (mg/L);

\( C_o \) the initial chlorine concentration (mg/L);

\( COD\textit{Mn} \) permanganate index (mg/L);

\( DBPs \) disinfection by-products

\( GAC \) Granular activated carbon

\( k_1 \) the first-order rate constant for slow reactions (1/h);

\( k_2 \) the first-order rate constant for rapid reactions (1/h).

\( K \) constant that is function of initial concentrations of substances A and B and their coefficients

\( M \) positive component of rate constant (1/t)

\( PAC \) Powdered activated carbon

\( R^2 \) Correlation coefficient

\( RMSE \) Root mean squared error

\( THM \) Trihalomethane (μg/l)

\( x \) the fraction of the chlorine demand attributed to slow reactions;
Chapter I : Introduction and objectives

Introduction and objectives

1.1. Background Summary

One of the important aspects of water quality in regard to water treatment is disinfection, particularly by chlorination. This is usually done to remove pathogens and other health-related micro-organisms. Chlorine is widely chosen as a disinfectant in drinking water utilities due to its low cost and long-lasting affect. In water distribution network chlorine concentration decreases due to its reactions with organic and inorganic compounds present in the different surface and subsurface water sources, and due to its interaction with deposits and biomass at the inner pipes walls and with the pipe wall material. Therefore, understanding the factors that causes the loss of chlorine is a requisite to maintain sufficient chlorine residual levels in distribution systems and to meet the required regulations and satisfy the customer s’ need.

On the other hand, application of chlorination and the presence of chlorine residuals lead to the formation of potentially harmful disinfection by-products (DBPs) in the treated water. These by-products result due to chlorine reactions with the organic matter contained in water resource. The focus on the occurrence of DBPs in drinking water systems has increased from the ’70s, and special attention has been paid to the concentration of trihalomethanes (THMs), adsorbable organic halide (AOX) and other DBPs due to its influence on human health.

Effective monitoring, and more importantly, 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. Such models are currently used for dosage optimization, chlorination facilities siting and prediction of critical locations where chlorine may decay to ineffective levels.

The main purpose of this study was investigation the effect of biofilm on chlorine decay in water distribution network of defined case study area after applying cleaning process on its pipe network. During the initial investigation, it was found that chlorine
Chapter I : Introduction and objectives

degrades rapidly after water leaves the water treatment plant of a new water supply network.

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.

Therefore, the reasons which lead to this fast decay of chlorine have been studied, in particular the effects of the applied water treatment process (biological ammonium removal).

1.2. Objectives of the research

The main objectives of the research are:

- Investigating the influence of biological ammonium removal on the bulk chlorine decay and disinfection by-products.

- Determination the influence of different factors on the reactivity of chlorine in bulk water by performing a series of experiments on water samples collected from water treatment plant

- Evaluation existing kinetic chlorine decay models in term of their potential to properly predict the chlorine residual in bulk water.

- Estimating and comparing the ability of parallel first order model and second order model in predicting the bulk chlorine residual in several water samples with different organic matter contents and with a wide range of initial chlorine concentrations

- Developing of mathematical models for the bulk chlorine coefficients of each model as a function of initial chlorine concentration and organic matter.
Literature review

The purpose of this review is to give an overview of chlorine decay in water supply system. This chapter will initially discuss the background information of chlorine decay kinetics. The importance and formation of disinfection byproduct (DBP). The final part of this chapter will summarize the literature review of chlorine decay modelling in distribution systems.

2.1 Kinetics of chlorine decay

Chlorine is commonly added to water before it leaves the utility plant to provide residual disinfectant in distribution networks. However, their concentration and thus their effectiveness decrease as water flows through the distribution network due to several factors. During water treatment process in treatment plants, chlorine is applied in the form of compressed gas or as a solution of sodium hypochlorite (Harp, 2002). Chlorine gas reacts with water to produce the disinfectant HOCl (hypochlorous acid) as follow:

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \quad (2.1)
\]

Hypochlorous acid is a weak acid and will disassociate according to:

\[
\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \quad (2.2)
\]

HOCl and OCl\(^-\) ions are commonly referred to as “free available” chlorine. The concentration of each species at equilibrium depends on pH and temperature. In the pH range of 6.0 - 9.0 range, continuous transition between these two components can take place, and both hypochlorous acid and hypochlorite ions are present. At lower pH level hypochlorous acid, at higher pH level the hypochlorite ions predominate. Disinfection is more effective at lower pH levels, but the corrosion is liable to occur. Therefore, when using chlorine as disinfectant, the pH of the water should be in the 7.0-8.0 interval.

Similarly, aqueous solutions of sodium hypochlorite will hydrolyze according to:

\[
\text{NaOCl} \rightarrow \text{OCl}^- + \text{Na}^+ \quad (2.3)
\]
However, to achieve a balance between a chlorine dose and bacteriological quality of water, it is necessary to understand the mechanism of chlorine decay in water distribution systems and the factors affecting it.

In general, different kinds of reactions lead to the disappearance of chlorine (Gang et al., 2003): oxidation, addition and substitution. When oxidation of a substance by HOCl or OCl\(^{-}\) occurs, the C1\(^{+}\) radical accepts two electrons from the substance being oxidized to become a chloride ion (Cl\(^{-}\)).

In addition and substitution reactions, chlorine is added or substituted into the NOM molecular structure to form chlorinated organic intermediates, which might further decompose to form DBPs (Gang et al., 2003).

Only addition and substitution reactions produce chlorinated organic compounds. Oxidation reactions account for most of the "chlorine demand" of natural waters and waste treatment effluents (Jolley et al., 1978), but the end products are not chlorinated organic compounds. That is not to say that those products cannot be harmful.

2.2 Parameters affecting bulk chlorine decay:

As a relatively strong oxidizing agent, chlorine can react with inorganic and organic compounds present in the bulk water. As both organic and inorganic particles are present in varying concentrations and have different degrees of reactivity, the loss of chlorine over time is a gradual process. The half-life of chlorine in treated water (i.e. the time it takes for 50% of the initial chlorine to disappear) can vary from several hours to several days (Clark & Sivaganesan, 2002). Powell et al., (2000.a) studied the wall decay and bulk decay separately and observed a significant variation in the bulk decay constant (kb) with temperature, total organic carbon (TOC) and the initial chlorine concentration (Co).

2.2.1 Inorganic components

These substances may occur naturally in the water or may be anthropogenic in nature, such as ammonia (NH\(_3\)), halides (Br\(^{-}\) and I\(^{-}\)), SO\(_3^{2-}\), CN\(^{-}\), NO\(_2^{-}\), As\(^{3+}\), Fe\(^{2+}\) and Mn \(^{2+}\).

The important reactions that can effect chlorine decay are the reactions which involve ammonia or amino-nitrogen groups.

Chlorine reacts with different types of nitrogenous compounds such as ammonia, nitrites and amino acids. The reaction of ammonia with chlorine induce chloramine formation (Qiang and
Adams, 2004). Chloramines the sum of three different compounds: monochloramine (NH$_2$Cl), dichloramine (NHCl$_2$), and trichloramine (NCl$_3$), which are formed in a stepwise reaction as shown by Equations 2.4, 2.5, and 2.6:

\[
\begin{align*}
\text{NH}_4^+ + \text{HOCl} & \leftrightarrow \text{NH}_2\text{-Cl} + \text{H}_2\text{O} + \text{H}^+ \\
\text{NH}_2\text{Cl} + \text{HOCl} & \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O} \\
\text{NHCl}_2 + \text{HOCl} & \leftrightarrow \text{NCl}_3 + \text{H}_2\text{O}
\end{align*}
\]

The trichloro-amine compounds are instable, and decompose to nitrogen gas (N$_2$). The formed chloramine gives an unpleasant odor to the treated water. Different factors influence these reactions such as the chlorine: ammonia nitrogen ratio, pH, temperature, and contact time. Ammonia is sometimes removed from the water at a water treatment plant (WTP) to ensure the efficiency of chlorination. Ammonia removal methods can be either breakpoint chlorination or biological filtration which is applied in the studied WTP in this work.

On the other hand, chlorine can oxidize ferrous ion (Fe$^{2+}$) that exists in groundwater to ferric ion (Fe$^{3+}$). The reaction is dependent on the pH of the water as the overall reaction rate increased with increased pH (Eq 2.15). Likewise, chlorine oxidizes manganese compounds that precipitate as manganese dioxides. Manganese reactions proceed over a range of pH 7 to 10, and the optimum being the higher values.

The reaction of free chlorine and manganese is shown in Equation 2.8, the reaction is very rapid and no residual is observed until all manganese is eliminated.

\[
\begin{align*}
2\text{Fe}^{2+} + \text{HOCl} + \text{H}^+ & \rightarrow 2\text{Fe}^{3+} + \text{Cl}^- + \text{H}_2\text{O} \\
\text{Mn}^{2+} + \text{HOCl} + \text{H}^+ & \rightarrow \text{Mn}^{4+} + \text{Cl}^- + \text{H}_2\text{O}
\end{align*}
\]

Other kinds of inorganic compounds that react with chlorine are hydrogen sulfide gas. Hydrogen sulfide gas sometimes present in groundwater and its reaction with chlorine forms sulfur or sulfate.
2.2.2 Organic compounds

The reactions of chlorine with organic matter makes up the majority of the chlorine demand (Clark & Bouton, 1998). A relationship between organic matter concentration and chlorine decay would therefore be expected.

In general, free chlorine reactions with organic matter include substitution (hydrogen by chlorine), oxidation (oxidation till CO$_2$ or only partial oxidation) and addition to multiple bonds. Addition reactions with free chlorine could be significant in waters containing highly unsaturated plant pigments. However, the partial oxidation is the main component of chlorine consumption in bulk water (Kastl et al. 1999). In some cases, the disinfection by-products (DBPs) are formed due to reaction the organic matter (NOM) with chlorine. The types and concentrations of DBPs formed during water treatment are affected by several water quality factors, including the characteristics of natural organic matter in the water system, type and dose of disinfectant, contact time, temperature, and pH.

2.2.3 Initial chlorine concentration

Previous experimental studies have shown an inverse relationship between the rate of bulk chlorine decay and the initial chlorine concentration, when tests were conducted on the same waters under identical laboratory conditions (Dharmarajah et al., 1991; Zhang et al., 1992; Powel, 1998; Hua, 1999; Hallam, 2000; Vieira et al., 2004; Warton, 2006).

In addition, some physic-chemical input parameters (e.g. temperature, turbidity and flow) were also assessed as they can affect chlorine decay (Cordoba et al., 2014).

Various researchers had investigated the effect of pH on chlorine decay. Zhang and Andrews (2012) found no statistical difference in chlorine decay rates among samples treated at three pH values (6.6, 7.6 and 8.6) with pseudo-first-order decay constants of 0.0018, 0.0022, and 0.0022 h$^{-1}$ respectively. Qualls and Johnson (1983) failed to observe expected differences in the rats across a pH range of 6.5e8.0.

2.3 Parameters affecting wall chlorine decay

Chlorine disappears due to a combination of processes at the pipe wall (Devarakonda et al., 2010). These processes include reactions between chlorine and biofilms attached to the distribution pipe wall, accumulated sediments, corrosion process, and mass transport process of chlorine and other reactants between the bulk flow and pipe wall.
Chapter II : Literature Review

The pipes normally used in distribution systems can be classified in two main groups: synthetic pipes and metallic pipes. According to its reactivity, pipes can generally be classified into reactive pipes (unlined iron) and unreactive pipes (PVC, MDPE, cement-lined iron). Hallam et al. (2002) found that the pipe material has a strong influence on the wall decay during distribution. Previous studies have reported that synthetic materials such as PVC, medium and high-density polyethylene, cement lined iron and polypropylene have a very low chlorine demand (Kiéné et al. 1998).

Metallic pipes have high chlorine demand and chlorine decays as chlorine reacts with the elemental metal or the associated corrosion products on the pipe wall, especially in unlined cast iron pipes. Powell et al. (2000.a) reported the factors which control wall chlorine decay through field surveys several distribution pipes. It can be specified that majority of the factors which have been shown to influence the wall decay are:

- Pipe material and diameter (Sharp et al., 1991);
- Initial chlorine concentration (AWWARF., 1996);
- Corrosion (Kiene L et al., 1998);
- Biofilm and flow rate (velocity)

As a result, chlorine will either decay due to reactions with compounds contained within the bulk water or due to reactions at the pipe wall. Hallam et al., (2002) found that bulk decay may be isolated from wall decay by carrying out chlorine decay experiments on the source water under controlled conditions in laboratory.

2.4 Disinfection by-products formation

The natural organic matter (NOM) in water reacts with chlorine during the disinfection process, which forms disinfection byproducts (DBPs), (USEA., 2006). Disinfection and disinfection byproducts formation are considered as a coupled phenomenon. In 1974, Rook discovered that hypochlorous acid and hypobromous acid react with naturally occurring organic matter to create trihalo methanes (THMs).

Natural organic matter (NOM) constitutes the major component of total organic carbon (TOC) in most water. NOM is a heterogeneous mixture of complex and mostly
macromolecular organic materials, including humic substances, hydrophilic acids, proteins, lipids, carboxylic acids, polysaccharides, amino acids, and hydrocarbons (Thurman, 1985; Lenheer and Croue, 2003).

The formation of DBPs depends primarily on source water quality characteristics and on the location in the treatment process where disinfectants are added. The most important water quality parameters include the nature and concentration of organic precursor materials, water temperature, pH, conditions under which the disinfectant is used, such as the disinfectant dose, point of addition, contact time, and residual disinfectant concentration (Roberts et al., 2002).

Rook’s discovery of THMs in drinking water led to research on other chemicals formed when chlorine is added to water, and to the health effects of these chemicals. Up to 700 different types of DBPs have been observed in the chlorinated water, such as trihalomethanes (THMs), haloacetic acids (HAAs), adsorbable organic halides (AOX), haloacetonitriles, haloketones, and other known and unknown compounds. (S.D. Richardson, 2003). Some of these DBPs are human carcinogens and have chronic and sub-chronic effects to human health (Health Canada, 1996; Hrudey, 2009; King et al., 2000; Mills et al., 1998).

As chlorinated organic compounds, trihalomethanes (THMs) and haloacetic acids (HAAs) are considered dominant in drinking water distribution systems. Considering the severe health impacts of THMs, a lot of regulations in most countries have been formulated and reevaluated time to time for controlling and regulating concentration of THMs in drinking water supplies. THMs are often used as indicators of total disinfection by-product formation (Kitis et al. 2001).

Formation of THMs varies spatially and temporarily within water treatment plants and distribution systems. The variability may be attributed to the source water quality, variation in the pretreatments, local environmental conditions, and dynamic nature of DBPs formation in the treatment plants and distribution system.

Hydrophilic acids, humic substances, and organic compounds are the primary precursors of THMs (Roberts et al., 2002). The presence of nitrite is considered as one of the precursors for THMs; however, other researchers proved that it did not have any significant effect on THM
Chapter II: Literature Review

formation (Hu et al., 2010). Besides the mentioned precursors, if bromide is present in the water, the available chlorine in the form of hypochlorus acid can react with bromide to form hypobromous acid. These reactions will eventually result in the reaction of the precursors with the formed hypobromous acid causing the formation of chloro-bromo THMs (Liang and Singer., 2003).

THMs have the general formula CHX₃, where X can be Cl or Br. The most common THM compounds are dibromochloromethane (CHClBr₂), bromoform (CHBr₃), chloroform (CHCl₃), and dichlorobromomethane (CHCl₂Br). The sum of these four compounds is referred to as Total Trihalomethanes (TTHMs). Among the mentioned THMs, those which are associated with bromide are considered as brominated THMs, while those which do not have a bromide ion as a precursor are chlorinated types of THMs. Song et al., 2010) found that THMs have higher formation potential with the increase in NOM and chlorine dose, and some other research also concluded a strong correlation between TOC concentrations and THM formation with R² = 0.90 (Uyak et al., 2005).

It has been a challenge for drinking water treatment plants to simultaneously minimize the risk of DBPs formation and provide sufficient chlorination to avoid further activities of microorganisms in distribution systems. The health risks from these byproducts at the levels at which they occur in drinking water are extremely small in comparison with the risks associated with inadequate disinfection. Thus, it is important that disinfection not to be compromised while attempting to control such byproducts.

2.5 Treatment process of ammonium removal

Although ammonium in water does not pose a direct health concern, nitrification of significant amounts of excessive ammonia may. Uncontrolled nitrification may result in the accumulation of nitrite (Holt et al. 1995), which is very dangerous for humans. In addition, nitrification in drinking water systems leads to ineffective disinfection when chlorination is applied and corrosion of metal pipe material. Therefore, sufficient ammonium ion removal is needed when chlorination is applied for disinfection.

There are different physicochemical methods for ammonium removal, such as break-point chlorination, ion exchange, reverse osmosis, and electrodialysis. The traditional method for ammonium removal is breakpoint chlorination.
One of the significant disadvantages of breakpoint chlorination is the formation of disinfection by-products such as trihalomethanes (THM) and adsorbable organic halides (AOX) compounds, particularly when the required chlorine dose is high (Kollar and Ribar. 1991). Therefore in most of cases, activated carbon adsorption is required as treatment technology step of before the final disinfection step in order to remove disinfection by-product before pumping the treated water to the distribution network.

Recently, another technology has been widely applied in several water treatment plants to remove ammonium from source water. This technology which defined as the biological ammonium removal, is usually a two-step process in which sequential oxidation of ammonia into nitrite and then nitrite into nitrate occurs. Ammonia and nitrite oxidizer communities spontaneously grow on the filtration material used in drinking water filters (Laurent et al. 2003). Different factors affect the biological nitrification in drinking water treatment, such as intensity of aeration, nitrifying bacteria, temperature and pH, etc....

Aeration is a necessary feature of any biological ammonia treatment system. The amount of oxygen that can be added to the water is controlled by the saturation limit of oxygen in water. The biological nitrification appears to be more efficient than break-point chlorination, cost-effective (Konrád, 2012).

2.6 Treatment process of organic matter removal

As it mentioned previously, natural organic matter (NOM) is the precursor for the key disinfection by-products (DPBs) following chlorine disinfection (Zeng and Arnold, 2014). Therefore, the content of NOM has to be reduced before the disinfection step to avoid the formation of these by-products (DPBs).

Different types of treatment are used to remove the NOM from water. The most common treatment consists of coagulation-flocculation-sedimentation, rapid sand filtration and disinfection. In addition to other treatments such as activated carbon adsorption, ion exchange, electro-coagulation, bio-filtration, membrane filtration, sonochemical, and advanced oxidation. (Owen et al., 1995).
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2.6.1 Coagulation
Most treatment plants optimize their coagulation process for turbidity (particle) removal. However, coagulation processes can also be optimized for natural organic matter (NOM) removal with higher doses of inorganic coagulants (such as alum or iron salts), and optimization of pH. The Coagulants are added to water to induce dissolved and colloidal species to agglomerate into larger particles known as flocs. These flocs are removed in a clarification step, which may be based on gravity or buoyancy.

The effectiveness of coagulation to remove NOM and particles depends on several factors, including coagulant type and dosage, mixing conditions, pH, temperature, particle and NOM properties (such as size, functionality, charge and hydrophobicity) (Jarvis et al. 2004), as well as the presence of divalent cations and concentrations of destabilizing anions (bicarbonate, chloride, and sulfate) (Sharp et al. 2006, Duan and Gregory, 2003)

2.6.2 Adsorption
Activated carbon (AC) (both granular activated carbon (GAC) and powdered activated carbons (PAC)) can be used to adsorb soluble organics that may react with disinfectants to form byproducts. The adsorption concept of activated carbon primarily is a physical process in which dissolved contaminants adhere to the porous surface of the carbon particles. The extent of the adsorption depends on a number of factors such as charge, size and polarity of the adsorbate, and the relationship between the adsorbate structure and the activated carbon surface.

The adsorption behavior of NOM is particularly difficult to understand due to its heterogeneous nature (Newcombe, 1999). Newcombe et al. (2002) showed that the adsorption of NOM is controlled predominantly by the relationship between the molecular size distribution (MSD) of NOM and the pore size distribution of the carbon.

On the other hand, previous studies have shown that coagulation prior to the granular activated carbon (GAC) filtration removes particles that might clog the GAC filter and also can remove NOM, which reduces the loading on the GAC filters (Jacangelo et al., 1995). Semmens et al (1986) and Hooper et al (1996) found that coagulation can significantly increase both bed life and the adsorptive capacity of NOM on GAC.

Laine et.al, (1990) argued that PAC adsorption is a better option compared to coagulation as a pretreatment of ultrafiltration (UF). Uyak.V.et al (2007) found that supplementing enhanced
coagulation with PAC adsorption increased the removal of DOC to 76%, and PAC adsorption removed mostly low molecular weight and uncharged NOM substances.

2.6.3. Membrane Technology

Membranes, which used historically to desalinate brackish waters, have also demonstrated excellent removal of natural organic matter. Membrane processes use hydraulic pressure to force water through a semi-permeable membrane that rejects most contaminants. Variations of this technology include reverse osmosis (RO), nanofiltration (low pressure RO), ultrafiltration and microfiltration (comparable to conventional sand filtration). Previous studies (Taylor et al., 1987; Fu et al., 1994) have shown that NOM can be effectively rejected during filtration by low and medium pressure membranes, including nano filtration (NF) and, to a lesser extent, ultrafiltration (UF).

Other conventional methods of reducing DBP formation include changing the place of chlorination and using chloramines for residual disinfectant. EPA predicts that most water systems will be able to achieve compliance with new DBP regulations through the use of one or more of these relatively low cost methods. Water system managers may also consider switching from chlorine to alternative disinfectants to reduce formation of THMs and HAAs. However, all chemical disinfectants form some DBPs.

2.7. Modeling of chlorine decay

Modelling of water quality in distribution systems has become necessary to understand the problem of water quality at the consumer's tap. This option has effectively reduced the cost of studying the spatial and temporal variation of a number of water quality constituents including chlorine (Grayman et al., 1999).

Numerous factors contributing to chlorine decay in the water distribution system have been identified, including the pipe wall material, the total organic carbon (TOC), the temperature and the pH (Kiene et al., 1998). Therefore, to ensure the preservation of chlorine residual throughout water distribution systems, the need exists for accurate chlorine decay modelling in the water distribution systems.
Previous studies have developed kinetic-based and mechanistic-based models to predict bulk chlorine fate within the water distribution system (WDS). These models are typically based on many parameters including organic carbon content, ultraviolet absorbance (UV254), temperature, and pH. (Chowdhury, Champagne, & McLellan, 2009).

Although many efforts have been made in the last decades (Shang et al., 2008), the modelling of chlorine residuals is still complex, as it relies on the accuracy of hydraulic models to describe flows and flow velocities (Blokker et al., 2008) and on the adequacy of chlorine decay kinetic models (Fisher et al., 2011a).

Models that simulate chlorine decay are currently used for dosage optimization, chlorination facilities siting and prediction of critical locations where chlorine may decay to ineffective levels (Monteiro et al., 2014).

Most kinetic models describing chlorine decay have been established empirically or semi-empirically. A basic issue of using decay equations is determination of the decay constants, which can vary with the quality of the source water, its temperature, and the material properties of water pipes (Kowalska, 2006).

The chlorine concentration after the WTP decreases gradually as the treated water goes through the pipe network. The reaction rates of chlorine are dependent on several factors such as source water characteristics, treatment type (which can affect the amount and type of reactive material available for reaction), contact time (both in the treatment plant and distribution system), and the characteristics of the distribution system (e.g. pipe material, pipe age) (Dominic et al., 2003).

Chlorine consumption could be mainly divided by bulk chlorine decay and wall decay. The bulk decay is due to chlorine consumption with organic and inorganic matters, and the wall decay is due to reactions of chlorine with pipe materials, biofilms on inner pipe walls and so on.

The total decay constant \( k \) is often expressed by the decay due to the chlorine demand of the pipe (known as the wall decay constant \( k_w \)) and the decay due to the quality of water itself (known as the bulk decay constant \( k_b \)) (AWWARF., 1996). The overall chlorine decay expression postulated for water flowing through a distribution system is shown in Equation (2.9):
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The bulk chlorine decay rate can be obtained by experiments and the wall decay rate can be estimated by calibration, where the results from a simulated network model compared with the results measured in a distribution system.

It becomes important to accurately model the bulk-decay first, as it depends only on the quality of the transported water, and it is independent from the system. In contrast, the wall decay can only be quantified as differences between the system measurements of chlorine and the calculated values from the bulk-decay model at corresponding points and times (Fisher et al., 2011).

One of the advantages of the separate estimation of bulk and wall decay is the separation of water characteristic from system characteristic, so that changes to water paths, pipe networks and reservoirs do not require changes to the bulk reaction model parameters in different system scenarios.

Reviewing the literature, number of models has been developed to predict chlorine decay in drinking water. These models could be classified into three different categories:

2.7.1 Single-constituent decay models

The most popular model which used by Johnson (1978) depends on this concept is the first-order decay model in which the chlorine concentration is assumed to decay exponentially as it can be seen in Eq (2.10):

\[
\frac{dC_{Cl}}{dt} = -k * C_{Cl} \tag{2.10}
\]

Where, \( C_{Cl} \) is chlorine concentration [mg/L], \( k \) is the bulk decay rate constant [1/h], \( t \) is the time [h]. The general analytical solution for the first order kinetic model is expressed as follow in Eq (2.11):

\[
C_{Cl} (t) = C_{Cl0} * \exp (-k * t) \tag{2.11}
\]
Where, $C_{Cl}(t)$ [mg/L], is the chlorine concentration at time $t$, $C_{Cl0}$ [mg/L] is the initial chlorine concentration at time $t=0$, and $k$ is the first order decay constant [h$^{-1}$].

Equation (2.12) describes the rate of a first-order reaction, as it is proportional only to the chlorine concentration. The simplicity and easiness of this model made it widely used for prediction of chlorine residual (mainly because it has an analytical solution and requires only one parameter to be determined). Unfortunately, the first order model has not presented a good data fitting in many applications. The dependency of disinfectant decay rate ($k$) only on the disinfectant concentration, means that the model often does not accurately describe chlorine decay in water distribution systems. If the chlorine dose is varied, $k$ needs to be varied substantially to obtain any reasonable fit to the data.

Various attempts have been made to improve the accuracy of the first-order model. Haas and Karra (1984) compared the performance of the first-order model with alternative kinetic models, which also described decay rate as a function of chlorine alone. These were the $n^{th}$ order model where the decay rate in this model is proportional to $n^{th}$ power of chlorine concentration, limited model which assumes that some of the chlorine do not react and remains in the water and the parallel first-order model (Eq. 2.13) that comprising two kinetic terms of chlorine decay.

The parallel first-order model represents rapid and slow decay, where both occurring at the same time and according to a first-order reaction. A fraction of the initial chlorine concentration ($x$. $C_{o}$) decays with rate constant ($k_{1}$) and the remainder $[(1-x) C_{o}]$ decays with different rate ($k_{2}$).

Table (2.1) presents the kinetic models and their corresponding parameters for prediction of chlorine decay in water distribution systems.

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>The differential form</th>
<th>the integrated form</th>
<th>coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n^{th}$ order model</td>
<td>$dC/ dt = - k C^{n}$</td>
<td>$C_{(t)} = (kt (n-1) + (1/C_{o})^{(n-1)} t^{-1})^{1/(n-1)}$</td>
<td>$k , n$</td>
</tr>
<tr>
<td>limited first order model</td>
<td>$dC/ dt = - k (C - C^{*})$</td>
<td>$C_{(t)} = C^{<em>} + (C_{o} - C^{</em>}) exp (-k t)$</td>
<td>$k , C^{*}$</td>
</tr>
<tr>
<td>parallel first order model</td>
<td>$dC/ dt = - k_{1} C_{1} - k_{2} C_{2}$</td>
<td>$C_{(t)} = C_{o} x exp (-k_{1}t) + C_{o}(1-x)exp (-k_{2} t)$</td>
<td>$k_{1}, k_{2}, x$</td>
</tr>
</tbody>
</table>
Vasconcelos et al. (1996) compared these models on data from 11 sites taken from five different drinking water systems in the United States. They concluded that, although the parallel first-order model performed best, it was not worth the additional effort required. However, seven of the initial chlorine concentrations were less than 1 mg/L, so that the initial decay (faster than first order) may not have been well represented.

Powell et al. (2000b) also compared the same models to two additional models (except for the \(n^{th}\) - order with stable component) on over 200 samples taken from 32 locations in the Severn Trent, England, considering a wide range of temperatures. Their conclusion showed that the performance of the first- and second-order models (with respect to chlorine) were worse than other models in the worst 10% of cases fitted with each mode. As well, Vieira et al. (2004) compared the same models used by Powell et al. (2000b). They found that the parallel first-order model was superior to all others tested, to describe chlorine decay in the untreated groundwater supplying Almada, Portugal.

However, none of the studies related to the models of Haas and Karra (1984) restrict the values of the parameters to obtain the best fit to each decay test. Kiene et al. (1998) found that the kinetic constants for reactions in the bulk liquid to be dependent on the water quality parameters such as temperature and organic content of the water. In fact, the concepts of these models depend either on the assumption that the effect of reacting agents is neglected or on that the concentrations of these reacting agents are much larger than chlorine. Therefore, it is assumed that the reaction rate is only proportional to the chlorine concentration. However, this assumption is not necessarily valid for all applications.

2.7.2. Two-constituent decay models

A second-order kinetic approach has also been studied by Clark (1998). In this case, the concept of the model is based on the reaction between chlorine and another notional substance. The balanced reaction equation can be represented by:

\[
aA + bB \rightarrow pP
\]  
\[(2.12)\]
Where A is the chlorine component, B is the reacting substance, P is the disinfectant by-product component, and a; b; and p are stoichiometric reaction coefficients. Clark assumed the reaction rate to be first-order with respect to A and B; and second order overall,

\[
\frac{dc_A}{dt} = -k_A C_A C_B, \quad \frac{dc_B}{dt} = -k_B C_A C_B
\]  

(2.13)

Where \( C \) and \( k \) are the concentration and decay rate coefficient for the disinfectant (subscript A) and reactive component (subscript B), respectively, and \( k_B = \frac{b}{a} k_A \). While the reactive component is unknown, the initial concentration \( C_{B,0} \) must also be incorporated in the estimation process. Clark (1998) equated the amount of A that reacts in a given time to the equivalent amount of B as the following:

\[
C_B = C_{B,0} - (C_{A,0} - C_A) = C_A - (C_{A,0} - C_{B,0}) = C_A - C_D
\]  

(2.14)

Where:

\[
C_D = C_{A,0} - C_{B,0}
\]  

(2.15)

Substituting Equation (2.15) into Equation (2.16) and integrated the result, the following equation for chlorine concentration at any time \( t \) is given by (2.18):

\[
C_A(t) = \frac{C_{A,0} (1-K)}{1-K e^{-ut}}
\]  

(2.16)

Where:

\[
u = M (1 - K),
\]  

(2.17)

\[
K = \frac{aC_{B,0}}{bC_{A,0}}, \quad M = \frac{\beta K_A C_{A,0}}{\alpha},
\]  

(2.18)

\( M >0, \ K \) (dimensionless) and \( M (1/T) \) must be estimated.

Clark (1998) showed that the second-order model was at least as good as the parallel first-order and \( n^{th} \)-order formulations tested by Vasconcelos et al. (1996) using the same data.

Huang and McBean (2007) attempted to confirm that Clark was wrong in deriving the Eq (2.17). However, Fisher et al. (2007) have been noticed after reviewing both papers, that the original formulation proposed by Clark was right except for missing a negative sign, which did not have any effect on the final result. As well, the solution of Huang and McBean (2007)
is incorrect because it did not impose the appropriate boundary condition after integration to obtain the particular solution.

Clark and Sivaganesan (1998) developed empirical regression models to estimate $K$ and $M$ that depend on natural water characteristics such as temperature, pH, TOC and the initial chlorine concentration ($C_o$). They explained 71% and 78% of the variance in $K$ and $M$, respectively, from their relationships with water characteristics.

Boccelli et al (2003) noticed that these resulting regression equations of Clark and Sivaganesan were inconsistent with the theoretical relationships of $K$ and $M$ provided. Also they extended the Clark (1998) model to examine the effect of successive rechlorinations on chlorine decay (and trihalomethane formation) on waters from five different resources. They showed that the second-order model did not adequately describe the decay behavior after a single chlorine dose (up to 3 mg/L) over the full range of time of measurements (mostly 5 days) with discrepancies increasing with initial dose.

G. Kastl et.al (1999) found that there are two disadvantages for the second order model: one is that the proposed analytical solution is only valid when $C_{A,0} \neq C_{B,0}$, and if not, the formula should be changed to Eq (2.19):

$$C_A(t) = \frac{C_{A,0}}{(1 - C_{A,0} * k * t)}$$

The second disadvantage is that it considers only one individual species to react with chlorine. This is important as in most cases at least two different reactions occur with chlorine, the initial fast reaction and later the slower one.

Dominic (2003) found that the second-order chlorine decay model, like the first order chlorine decay model (and most other decay models), was unable to adequately describe the initial rapid decay which generally occurred immediately after the initial chlorine dose was set. As a model for describing chlorine decay, the second-order model outperformed the first-order model and provided a framework to incorporate a reactive species.
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However, Fisher et al. (2011) argued the need for an accurate generic model of bulk decay, prior to any attempt to characterize the wall decay. Fisher et al. also pointed out that correctly partitioning chlorine decay in this way minimizes the effort required for calibration and scenario simulations to assist system planning/management.

2.7.3 Multiple reactive-constituent models

Multiple reactive-constituent models contain a rate equation for the increase in each constituent with time, which is generally some function of the concentrations of one or more of the constituents.

In fact, a multi-species approach to modeling is necessary to accurately describe the redox reaction involving hypochlorus acid (HOCl), hypochlorite (OCl⁻) and natural organic matter (NOM) (Shang, 2008).

Quails and Johnson (1983) presumed that chlorine depletion in bulk water is due to a series of concurrent reactions with a large number of different aqueous constituents, each of which might be expressed generally as follows:

\[ CI + X_i \xrightarrow{k_i} P_i \]  

(2.20)

Where, \( CI \) represents chlorine component, \( X_i \) the \( i^{th} \) fictitious reactive constituent and \( P_i \) and \( k_i \) are the assumed primary-product of the considered reaction and its reaction rate constant, respectively. Type and amount of \( X_i \) and their rate constants might be numerous different parallel reactions occurring simultaneously or consecutively.

Their model was for prediction of decay in the first 5 min after dosing, which was the time scale for cooling water to pass through a power plant. They considered that the NOM reacted with chlorine consisted of two types of compounds: fast- and slow reacting fulvic acids.

Kastl et al. (1999), developed the proposed model by Quails and Johnson (1983) and they suggested that all reactants with chlorine to be partitioned into two notional constituents: fast and slow reducing agents over the entire reaction time typical of distribution systems (up to 7 days).

In other words, they considered two parallel simultaneous reactions occurring between chlorine and two notional constituents in the water with the overall second order kinetics,
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assuming that one of the reactions is much faster than the other: Their reaction scheme can be expressed as follow:

\[
Cl_2 + \text{FRA} \rightarrow Cl^- + \text{inert products}
\]

\[
Cl_2 + \text{SRA} \rightarrow Cl^- + \text{inert products}
\]

(2.21)

Where FRA and SRA are the fast and slow reacting reducing agents in water, respectively. The agent concentrations are expressed only as equivalent amounts of chlorine with which they react. The second order reaction rates for the above-mentioned reactions in this model could be given as follows (2.22, 2.23):

\[
\frac{dC_{\text{FRA}}}{dt} = -k_{\text{FRA}} C_{\text{Cl}} C_{\text{FRA}}
\]

(2.22)

\[
\frac{dC_{\text{SRA}}}{dt} = -k_{\text{SRA}} C_{\text{Cl}} C_{\text{SRA}}
\]

(2.23)

Where \( C_{\text{FRA}} \) and \( C_{\text{SRA}} \) are concentrations of the two reacting agents (fast and slow), respectively.

Kastl et al. (1999) compared the performance of this model (parallel second-order model) with four others models. They showed that the two parallel reactant model was the simplest model to satisfy the criterion regarding invariance of coefficients in relation to initial dose (up to 4 mg/L), with the smallest weighted error.

As well, Kohpaei et al. (2011) compared the performance of first order model, second order model and parallel second order model for its accuracy. They found that second order model was better than first order one, but in the lower end of the decay curve the second order model predicted higher concentration. These findings indicated that water utilities will have trouble satisfying secondary disinfection goals or in identifying the effect of wall reaction on chlorine decay. In contrast, it was concluded that the parallel second order model is the most accurate modelling method among the three mentioned chlorine decay models, despite its complexity with four parameters compared to two parameters in second order model and one parameter in first order model.
Jonkergouw et al. (2009) defined a different term called the concentration-weighted average rate coefficient for all reactions with chlorine happening in the aquatic solution. They proposed an empirical equation for this coefficient with similar mathematical behavior. However, the efficiency of this model in accordance with its complexity is being questioned. They did not compare their approach with the more direct approach of simulating two or more reactants with chlorine by solving their respective rate equations simultaneously, which avoids a lot of problems.

As a result, the performance of chlorine decay models depends on good estimation of a number of chlorine decay parameters. In addition, a detailed hydraulic model of the system is required for accurate estimation of the residence time (Bowden. J et al.,2006).

2.8 EPANET :

EPANET is a computer program that performs extended period simulation of hydraulic and water quality behavior within pressurized pipe networks. EPANET was developed in 1993 with some kinetic models describing the decay of chlorine using data collected in field sampling studies (Vasconcelos., 1997). Hydraulic modelling should be first developed for predicting chlorine residual levels within a water distribution system using EPANET.

Chlorine decay theory (Ozdemir et al., 2002, Vieira et al., 2004, Nagatani et al., 2008), which is included in EPANET 2.0 help manuals and used during software quality analysis, account for both bulk and wall reactions.

Maier et al (2000) concluded that the EPANET model gives a better fit to the observations than the single decay coefficients when monochloramine decay was modeled in a 1.3 km water pipe. Nagatani et al (2008) found that EPANET predicted values, which were close to the observed values. In Portugal, it was stated that the contribution of wall decay reactions is more significant than bulk decay reactions after comparing EPANET results with real network samples (Castro et al 2003).
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Vasconcelos et al. (1997) indicated that chlorine kinetics can be effectively characterized as a combination of first order decay in the bulk liquid and first order or zero order decay reactions at the pipe wall. Rossman, (1994) provided a characterization of chlorine decay due to reaction with substances in the water (termed bulk decay) independently from the decay due to interaction with the pipe wall, biofilm adhering to the wall, and sediment deposited on it (termed wall reaction).

2.8.1 Bulk Reactions
Decaying of a substance while moving through a pipe can be generally described as an \( n \)th power function of concentration as shown in Eq. (2.24):

\[
    r = k_b C^n
\]  

(2.24)

Where \( r \) is the rate of reaction (mass/volume/time), \( k_b \) is the reaction constant, \( C \) is the reactant concentration (mass/volume), and \( n \) is the reaction order.

In practice, bulk decay coefficients can be determined by running a bottle test on the water entering the distribution system. The relationship between the bulk rate constant seen at one temperature (\( T_1 \)) to that at another temperature (\( T_2 \)) was expressed in EPANET using a van’t Hoff - Arrehnius equation of the form:

\[
    k_{b2} = k_{b1} \cdot q^{T_1-T_2}
\]  

(2.25)

Where \( q \) is a constant. In one investigation for chlorine, \( q \) was estimated to be 1.1 when \( T_1 \) was 20 °C (Koechling, 1998).

2.8.2 Wall Reactions
In EPANET 2.0, characterization of wall decay is provided by zero or first order kinetics (with respect to chlorine). It also included limitation of mass transfer to the wall.

Many factors can affect the rate of pipe wall reaction. These factors consist of the mass transfer coefficient which depends on the molecular diffusivity of the traced substance and the amount of wall area available for reaction.
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The wall reaction rate coefficient must be adjusted for mass transfer limitations that are dependent on the flow regime within the pipe segment. EPANET does this automatically, basing the adjustment on the molecular diffusivity of the substance being modeled and on the flow’s Reynolds number. For first-order kinetics, the rate of a pipe wall reaction can be expressed as:

\[ r = \frac{2 k_w k_f C}{R (k_w + k_f)} \]  

(2.26)

Where \( k_w \) = wall reaction rate constant (length/time), \( k_f \) = mass transfer coefficient (length/time), and \( R \) = pipe radius. For zero-order kinetics the reaction rate will be written as:

\[ r = \min \left( k_w, k_f C \right) \frac{2}{R} \]  

(2.27)

Where \( k_w \) now has units of mass/area/time.

The mass transfer coefficient has to be determined for the flow conditions. Thus, if it is assumed that chlorine reacts as it reaches the pipe wall and there is no accumulation (Rossman, 1994). Mass transfer coefficients (\( k_f \)), are usually expressed in terms of a dimensionless Sherwood number (\( Sh \))

\[ k_f = Sh \frac{D}{d} \]  

(2.28)

Where \( D \) = Molecular diffusivity of the species (in this case chlorine) being transported (\( L^2/T \)), \( d \) = Pipe diameter.

Currently, there is no established method for directly determining the kinetics of chlorine decay due to pipe wall reactions. Therefore, calibration against field data must be used instead.

Until recently, models of distribution system networks such as EPANET (Rossman, 2000) have only provided ways to implement one- and two-constituent representations of chlorine decay (with some restrictions). There is now available an extension to EPANET (MSX) that allows users to specify customized models of multiple reactive constituents within a network model (Shang et al., 2008).
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The combination of the EPANET and MSX toolkits allows for an efficient and flexible implementation of the model. By the EPANET-MSX system, the mathematical descriptions of fundamental water quality processes can now be translated to the scale of a water distribution network, without development of new algorithms or computer codes. Thus, EPANET-MSX provides additional motivation for research on water quality processes, and speeds the application of such research to study the evolution of drinking water quality in distribution systems (Shang et al. 2008).

Monteiro et al. (2014) showed that chlorine modeling with EPANET MSX is not as practical as standard EPANET 2.0, given the lack of a graphical user interface; in addition, calibrating a wall decay rate coefficient with MSX extension can be quite a time-consuming and complex task.

2.9 Summary and conclusions

In this chapter, initially, background information about the kinetics of chlorine decay and treatment processes of ammonium and organic matter removal were briefly discussed. As well, comprehensive literature review about chlorine decay modelling and factors effecting chlorine decay have been discussed.

Most of the studies proved the efficiency of biological ammonium removal in decreasing the ammonium concentrations of the treated water, but on the other hand, limited research has been carried out about the role of biological ammonium removal on disinfection by-products formation in drinking water system.

Therefore, in this research the effect of the biological ammonium removal on disinfection by-products formation will be investigated to have a better understanding of their relationship. Water quality data obtained from Hungarian water utility that applying biological ammonium removal technology will be analyzed, as well, to perform various laboratory experiments on collected water samples.
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Among all existing theoretical methods for bulk chlorine decay prediction, the most popular ones in the literature including first order reaction model, second order model, parallel first order approaches were paid more attention and compared more carefully.

The bulk chlorine decay rates have been observed to be affected by different factors. According to Powell et.al (2002), the dependency of bulk decay coefficients on temperature, UV, the initial chlorine concentration (Co) and total organic carbon (TOC) was noticed to be significant.

In this work, simple methodology was evaluated to incorporate the influence of organic matter content on chlorine decay modeling by determining the organic content in water with the permanganate index (COD$_{Mn}$) instead of the total organic carbon (TOC). This method is more feasible in waterworks, where there is no possibility for TOC measurement.

Some researchers developed mathematic equations in order to account for the combined effects of the natural water characteristics on the second-order model coefficients. It was noticed that the coefficient $M$ in Clark and Sivaganesan’s regression equations (1998) was independent of the initial chlorine concentration ($C_{A,0}$) and there was no dependency for this coefficient on the chlorine doses. Therefore, in order to clarify the relationship between these two parameters, comprehensive analysis was performed during this work.

However, further investigations and optimization is necessary in order to identify the limitations of the biological ammonium removal, and to predict the residual chlorine concentrations in water sample collected from water supply network and to test the second order model compatibility with hydraulic models, such as EPANET.
3.1 Introduction

In Hungary, one of the most significant quality problems of drinking water resources (Neunteufel R. and Laky D. 2009) are the ammonium, iron, manganese and arsenic content.

In this chapter, the methods and procedures for analyzing the samples will be explained. As well as, the influence of water treatment process (biological ammonium removal and UV-disinfection) and water quality parameters (initial chlorine concentration, inorganic and organic matter) will be investigated in order to develop empirically based models to relate functional dependencies.

3.2 Study Area

The studied water supply system in this work belongs to a small settlement situated in the east part of Hungary with population 4392 people (till the end of 2010). The water supply system consists of four wells (three of them are in operation), local water treatment plant (DWTP) with capacity of 1200 m³/day, two reservoirs (100 m³ and 200 m³ of volume) for the treated water, PVC and PE pipes with total length of 23 km and diameters range between 80-140 mm, Fig.3.1. The average daily consumption is about 580 m³/d. The study area was selected due to the installation of a new treatment process different than that was used six years ago; after mechanical cleaning of the pipes was carried out in order to remove the sediment and biofilm.

Fig 3.1: water distribution network of the studied settlement
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3.3 Treatment technology in WTP

In the studied distribution system, ammonium concentrations in the raw water vary between 0.61 mg/l and 1.42 mg/l, with an average of 1.06 mg/l. They are higher than the maximum allowable concentration value (0.5 mg/l) of deep confined aquifers which set by Government Decree 201/2001. As well as the mean iron and manganese concentrations in the raw water are 0.8 mg/l and 0.15 mg/l respectively, and they are slightly higher than allowable concentrations. Table 3.1 shows the maximum allowable concentration values of selected components according to the current Hungarian regulation (Government Decree No. 201/2001).

Table.3.1. the maximum allowable concentration according to the Government Decree 201/2001

<table>
<thead>
<tr>
<th>Components</th>
<th>Current limit according to Government Decree 201/2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium (ground water)</td>
<td>0.5 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>0.2 mg/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.05 mg/L</td>
</tr>
<tr>
<td>THM</td>
<td>50 µg/L</td>
</tr>
</tbody>
</table>

Before 2011, the applied treatment process in the studied water treatment plant was not able to remove and reduce ammonium concentrations, which were leading to form nitrite and nitrate in the studied distribution, system besides to the decrease of the disinfection efficiency, where ammonium reacts with chlorine forming chloramines.

Since November 2011, new treatment technology started operating in order to improve the water quality and to achieve effective removal for ammonium, iron and manganese. The previous treatment technology consisted of aeration and simple sand filtration treatment for the raw water. The new treatment process starts by 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 (Fig 3.2).
Chemical processes conventionally combined with filtration are used to remove ammonium from water, but these methods are sometimes costly and ineffective (Aboabboud et al. 2008). The biological ammonium removal is one of the applied methods that give another alternative for removing this pollutant from drinking water by biofilm processes. This technology depends on biological oxidation of ammonia (nitrification) to nitrite by Nitrosomonas bacteria and oxidation of nitrite to nitrate by Nitrobacter bacteria. By this kind of treatment, the nitrification in the distribution system and other problems associated with the presence of ammonia can be avoided.

At the studied water treatment plant, three fluidized bed reactors connected in series are used to achieve the biological ammonium removal Fig (3.3). Medium elements of these bioreactors are floating in flowing current of water and air bubbles to provide specific surface area for biofilm establishment. The bioreactors are backwashed daily and the effluent of this bioreactor is irradiated by ultra violet (UV) radiation as a sterilizer to achieve the biosecurity of water. UV lamps are distributed equally inside a tube (30 cm ID, 150 cm long). While the water flows through the tube, the UV light emitted from the bulbs inactivate the microorganisms and bacteria which yielded due to the biological nitrification in the bioreactors.
3.4 Analyzing the water quality data

Before starting the laboratory experiments, water quality data from routine sampling have been analyzed. These data were collected over ten years from 2003 to 2013. They included physical, chemical, and microbiological data such as temperature, ammonium, permanganate potassium consumption, free and total chlorine, THM, iron, manganese, arsenic, confirmed coliform failures.

These data were collected at different sites in the network and water treatment plant by the water utility. The water quality data were analyzed and checked by using excel application, knowing that there were periods of missing and erroneous values for some parameters.
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3. 5 Samples collection for investigation

All required samples were ordered to be collected from defined sections of the operated Water Treatment Plant (WTP). Then, the samples were stored in cleansed plastic containers of 20-litre volume, sealed properly and labeled to show all information about their sampling location, date and time. The samples were afterwards sent to the water laboratory of Sanitary and Environmental Engineering Department in Budapest University of Technology and Economics to be tested.

The processes of collections were repeated many times in different periods over two years to ensure the accuracy of the water quality parameters for each measurement.

3. 6 Location points of the Collected Samples

In order to investigate the effects of treatment changes in water quality characters, three points in the water treatment plant (WTP) have been selected to collect the samples.

- Raw water samples from wells (RW),
- Samples from the outlet of the Bioreactors and before the UV irradiation disinfection (BUW).
- Samples were taken upstream of the chlorination point after the treatment process (TW).

Every time and after collections the samples, they transferred directly from the site to the water laboratory to perform the tests. Once the samples were received, they were carefully poured into smaller glass containers of 5-litre volume and then kept in the laboratory fridges at 4ºC for the future use.

3. 7 Initial water quality analysis

To obtain the water characteristics, initial water quality testing for each water source was conducted before chlorinating the samples. This helps in understanding the composition of the water and thus helps explaining the chlorine decay behavior in each sample. The initial analysis consists of:

- Temperature measurements,
- Measurements of pH and conductivity,
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- Measurements of dissolved oxygen,
- Iron and manganese analysis,
- Ammonium measurement.

3.7.1 Temperature measurements

Temperature governs the rate of most chemical reactions that will occur in natural water systems and will also affect the nature and quantity of biological species present. The temperature readings of raw and treated water samples were taken using portable logging meter.

3.7.2 Measurements of pH and conductivity (EC)

pH value is intended to be a measure of the activity of hydrogen ions in solution. In water treatment, the measurement of pH is one of the most important and frequently tested parameters since many of the treatment processes involved are pH dependent.

A pH meter (pH / cond 340i) was used to measure pH levels in TW samples. Before using the meter, calibration of the meter electrode was run. For measuring the conductivity (EC) of TW samples an electrical conductivity meter was utilized.

3.7.3 Measurements of dissolved oxygen

After aerating the raw and treated water sample for 20 minutes in the laboratory, dissolved oxygen (DO) was measured by portable meter with optical dissolved oxygen probe.

3.7.4 Iron and manganese analysis

The determination of dissolved iron was performed in the laboratory according to Hungarian standards (iron: MSZ 448-4:1983), while manganese concentrations were determined according to the Hungarian standards (manganese: MSZ 1484 -2:1993). The detection limit for iron and manganese was 0.02 and 0.01 mg/L respectively.
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3.7.5 Ammonium analysis

Ammonium concentrations were measured in the laboratory of the University according to the standard method (ammonium: MSZ ISO 7150 -1:1992). The detection limit for ammonium was 0.01 mg/L.

3.8 Bulk Chlorine Decay and Organic Matter measurements

3.8.1 Chlorine dosing

To prepare the chlorine doses for chlorinating the samples, condensed sodium hypochlorite (15 g/l) was initially diluted to the desired level and then a defined amount of the resulted solution was used. First, 1 mL of condensed sodium hypochlorite which contains about 15 g of free chlorine was dosed into a 100 mL of deionized water to achieve 150 mg/L of free chlorine concentration. The diluted solutions of 150 mg/L concentration were prepared freshly every day when the experiments were carried out.

The next step was to calculate the volume of diluted chlorine solution, which was required to add to the water samples. The chlorine concentrations specified for testing the water samples ranged from 1.0 to 3.0 mg/L of Cl₂. For example, 8 ml of prepared chlorine solution (150 mg/l) was needed to dose 1000 ml of water sample in order to reach 1.2 mg/L of free chlorine as initial concentration.

3.8.2 Free chlorine measurement

Chlorine measurement techniques are generally divided into three groups; colorimetric, iodometric titration and amperometric methods. In this research, all free residual chlorine measurements were taken by using the DPD colorimetric method (4500-Cl.G) (Jae el al. 2012) and tio-acetil-amid was added to the samples to prevent combined chlorine formation.

However, due to the low concentrations of ammonium in the samples, it was found that combined chlorine concentrations were very low.

The following sampling procedure was used for all free chlorine measurements.
- Blank sample and chlorinated water sample were prepared by adding 5 mL phosphate buffer solution, 5 ml DPD indicator reagent and 0.5 ml of tio-acetil-amid to 100 mL deionized water in flask.
- The chlorinated water sample were measured by photometer (Nanocolor 400 D) at wavelength 540 nm.
- The detection limit for free chlorine was 0.1 mg/L.

3.8.3 Bottle test

The determination of bulk chlorine decay was carried out using the following procedure:

- All glassware was treated to ensure that any chlorine demand exerted by the glass had been satisfied.
- A 1 liter bottle was filled with water sample.
- Then the water was thoroughly mixed to ensure homogeneity for approximately 1 minute.
- As mentioned above in section (3.8.2), the water samples were dosed with chlorine by using sodium hypochlorite solution (150) mg/L after dilution to achieve various initial chlorine concentrations.
- The sample water was then decanted into 100 ml glass amber bottles that were sealed with plastic stoppers, ensuring only limited amount of air remained inside.
- All samples were stored in an incubator set to ambient temperature of the water sample during the investigations, which was about 20 °C.
- The chlorine concentrations within the bottle was then determined using the N,N-diethyl-phenylenediamine (DPD) colorimetric method (as detailed in section 3.8.2). The starting time and initial chlorine concentration were recorded.
- The measurements of free chlorine concentrations were performed at defined intervals and lasted until free chlorine concentrations reached 0.1 -0.2 mg/L.
3.8.4 Determination of Permanganate Index (COD$_{\text{Mn}}$)

Chemical oxygen demand (COD), which can indicate the level of pollution for water contaminated by reductive pollutants, is one of the most important measurable parameters for water monitoring (Hong et al. 2009). In this research, the organic content was indicated as COD$_{\text{Mn}}$ parameter.

Potassium permanganate KMnO$_4$ was used to measure the chemical oxygen demand (COD$_{\text{Mn}}$). Measured as the quantity of oxygen used for oxidation the organic compounds (mg O$_2$ L$^{-1}$), and is referred to as the Permanganate Index (EN ISO 8467).

3.8.5 Ultraviolet absorbance

The Ultraviolet absorption spectroscopy is measurement of the attenuation of a ray of light after it passes through a sample. This enables to determine the total amount of organic compounds in water by measuring the absorbance at a certain wavelength. The most common wavelengths for NOM measurements are from 220 nm to 280 nm (Ramuné el al.2012). The usual wavelength used for measuring UV absorbance is 254 nm), which corresponds to the strongest line of the emission spectrum of a low-pressure mercury lamp. UV254 absorbance indicates the concentration of organic molecules with aromatic groupings or extended conjugation (Edzwald, 1985).

In this study, UV absorbance of the treated samples by powder activated carbon (PAC) was performed using UV/Vis Spectrometer as follows:

- A quartz cell with 1.0 cm path length was used.
- Distilled water was used as the blank sample
- Water and blank samples were inserted into the sample compartment and the reference side.
- The applied wavelength of UV absorbance measurement was 254 nm.

3.8.6 Turbidity

Turbidity is the cloudiness or haziness of water caused by individual suspended particles, ranging in size from colloidal to coarse dispersions. The measurable proportion of the suspended matter in water, which interferes with light passing through
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it, is referred to as turbidity, and is usually measured in Formazin Turbidity Units (F.T.U) or Nephelometric Turbidity Units (N.T.U).

3.9 Investigation of factors affecting the bulk chlorine decay:

3.9.1 Effect of biological ammonia removal

To estimate the impact of biological ammonium removal technology on bulk chlorine decay, another ammonium removal treatment by zeolite filtration was applied on raw sample, and then it was chlorinated at laboratory.

During investigation the reasons of the extremely fast chlorine decay in bio-filtered samples, it was found that the concentrations of inorganic compounds were low so the main reason of chlorine consumption was the organic matter. Therefore, zeolite filtration was applied on water samples in order to compare between the biological ammonium removal technology and another ammonium removal treatment as zeolite filtration which does not has organic matter production.

The experiments started by collection of water from two points at the DWTP of the case study area. First, water from the influent of water treatment plant (raw water) and second, water from the downstream of bio reactors (BUW). Then, the samples were transported and stored at ambient temperature on the day of sampling.

Pilot experiments at laboratory were conducted by using natural zeolite filter to treat the raw water (RW). The used diameter of the zeolite grains ranged between 3 to 5 mm , placed into glass column (diameter = 4.5 cm ) and water was directed to the filter by using peristaltic pump.

First, The raw water was aerated and then pumped with flow rate 17.2 ml /min into the zeolite filter (high = 10 cm ) to provide enough contact time (Tc = 9.24 min) and then flowed upward through the zeolite layer. The effluent of the zeolite filter was collected in covered glass vessels. After filtration, dissolved minerals (Fe $^{2+}$, Mn $^{2+}$) and ammonium concentrations were measured in the filtered samples (FW) in accordance with the methodology outlined in section 3.7.3, 3.7.4 and 3.7.5 respectively. Later, both the FW and bio-filtered (BUW) samples were dosed with (1) mg/l of chlorine and the free residual chlorine concentrations were measured following the methodology
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described in sections 3.8.2 and 3.8.3 respectively. Then, the results of bulk chlorine decay in both samples were compared.

3.9.2 Effect of UV – irradiation disinfection

In the treatment plant, UV irradiation disinfection is applied after fluidized bed filtration in order to inactivate the organisms and bacteria.

To study the influence of UV disinfection on bulk chlorine decay, series of chlorine decay experiments were performed on water samples collected before and after UV irradiation unit. The pre-UV irradiation samples (BUW) were taken from the effluent of bio-filters before UV disinfection. Bottle tests were conducted over two-hour period on both samples, with varying the initial chlorine concentrations as follow: 1.1 mg/L, 1.2 mg/L and 1.5 mg/L. Free chlorine concentrations were measured at 5, 10, 15, 30, 45, 60, 90, 120, and 240 minutes from start of test, and then the results for each sample were compared.

3.9.3 Effect of initial chlorine concentration

Water was collected from the effluent of the studied water treatment plant before chlorination (TW). Then, the samples were dosed to achieve a certain initial chlorine concentration and tests were carried out following the methodology described in section 3.8.3. The applied initial chlorine concentrations were 1.2, 1.5, 1.8, 2.0, 2.5 and 3 mg/l.

Water samples were taken in order to measure the remaining free chlorine concentrations at intervals started from 5, 10, 15, 30, 45, 60, 90, 120, 240 minutes, etc, and lasted until obtaining free chlorine concentrations between 0.1 -0.2 mg/l, in accordance with the methodology outlined in section 3.8.2 and 3.8.3 respectively.

3.9.4 Effect of organic content

The effect of the natural organic matter (NOM) on bulk chlorine decay was investigated by performing different types of treatment processes at the laboratory in order to reduce and vary the organic content in treated water samples. These treatments were by:
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A- Powdered activated carbon (PAC)

To adsorb the organic compounds in the finished treated water (TW), 3 and 6 g of powdered activated carbon (PAC) were added to 500 and 1000 ml of TW samples respectively. Then, these samples were filtered through 0.1 μm membrane filter in order to remove powdered activated carbon particles and the organic material, which is adsorbed on PAC. To measure the effect of powdered activated carbon (PAC) on organic matter removal, ultra violet absorption at wave length of 254 nm (UV254) was conducted with a CARY 50 spectrophotometer for each sample before and after treating with PAC. As well as, the turbidity of samples was measured by electronic turbidity meter (430IR).

B- Granular activated carbon (GAC)

Another method to remove the organic matter from TW samples was applied at the laboratory by granular activated carbon (GAC) adsorption. Zeolite layer was laid under granular activated carbon layer in a glass column (diameter = 5 cm), then the finished treated water (TW) was pumped into the GAC column (high = 9 cm) by a peristaltic pump with flow rate about 20 ml /min. Applying up-flow filtration allows for longer contact time (Tc = 8.83 min) between the water and the activated carbon grains, and thus to increase the efficiency of organic matter removal. Fig 3.4

C- Coagulation

This method was also tested and applied to reduce the organic matter in the treated water of the water treatment plant. 300 and 200 ml of TW samples were coagulated by 8 mg/L and 12 mg/L of iron salts respectively and mixed rapidly for 4 min. Later, the samples were filtered by membrane filter (0.45 μm) to remove the iron salts. Fig 3.4

D- Dilution by distilled water

The water samples from effluent of water treatment plant (TW) were diluted by distilled water (DW) to vary the concentrations of natural organic matter (NOM) in the samples. First, CODMn concentration was measured in the treated water sample (TW), and then the TW samples were diluted by distilled water according to defined ratios. The distilled
water to treated water (DW: TW) ratios were determined as follows: 1:1, 1:2, 1:3, 2:1 and 3:1.

After applying the previous methods on the finished water (TW), the efficiency of the organic matter removal was investigated by measuring the chemical oxygen demand ($\text{COD}_{\text{Mn}}$) for each sample according to the method in section (3.8.4).

Finally, all samples after each treatment were chlorinated by using sodium hypochlorite solution according to the described methodology in section 3.8.3. The treated samples by PAC, GAC were chlorinated with various chlorine doses (0.5, 1.0, 1.2, and 1.5) mg/l, while two initial chlorine concentrations 1.2 and 1.5 mg/l have been used to dose each diluted sample. Then, the residual free chlorine concentrations were measured as it was described in the section 3.8.2.

![Fig.3.4. photos from laboratory experiments](image)

**3.10 Methodology of chlorine decay modeling**

Several models for predicting the decay of residual chlorine have been tested in this work to predict the residual chlorine concentrations.

First, the single-constituent decay models which have been described earlier in the section 2.7.1, were applied on the experimental data that have been obtained during the free chlorine measurements, after defining the better fitting model between the
measured and predicted data, the model coefficients were estimated by optimizing their values to minimize the sum of the squared errors between the modelled and observed chlorine concentrations.

Further, the effects of water quality parameters on model coefficients were studied by plotting each coefficient versus the independent variable of the water quality.

In addition, the two-constituent decay which is the second-order model (Eq.2.14) was examined on the same experimental data to consider the influence of reactant constituents. Also, the ability of this model in fitting between the measured and modelled data was investigated, the model coefficients were defined, and the relationship between the water quality parameters and the model coefficients were studied.

To describe the behavior of the selected model coefficients, various empirical equations have been tested to determine the coefficients of each model as functions of water quality parameters. Statistical measures such as the determination coefficient ($R^2$) and the root-mean-square error (RMSE) for the assessment of the correlation between predicted and measured data values were obtained.

Last, the accuracy of the analytical solution in coefficients estimation for different series of chlorine decay data sets was evaluated. Independent set of chlorine decay data which obtained from the laboratory experiments have been used to validate the proposed model.
Chapter IV: Evaluation of available water quality data and laboratory experiments

**Evaluation of available water quality data and laboratory experiments**

4.1 Introduction

In this chapter the factors that impact the bulk chlorine decay will be evaluated and studied. It consists of two sections: in the first one, the water quality data will be evaluated and discussed, while in the second section, the results of laboratory experiments are presented.

4.2 Evaluation of water quality data

Analyzing of water quality data (provided by the water utility) of the studied area shows decrease in iron and manganese concentrations in the network after applying the new treatment technology in 2011, see Fig.4.1.

The concentration of ammonium reduced significantly in the treated water since 2011, the date of operation the biological ammonium removal, as it can be seen in Fig 4.2.

On the other hand, gradual increase in THM concentration was observed in the pipe network after the starting with the new treatment process, as shown in Fig.4.3. However, the increased values still did not exceed the Hungarian Standard limit of THM concentration, which is 50 μg/L (Table 3.1). One of the reasons that may be attributed to this increase is existence of free chlorine in the system after applying the new treatment process. Before that, combined chlorine (chloramine) was dominant in the system due to the presence of ammonium ion in the treated water. It can be also seen from Fig 4.4 that organic content at the effluent of WTP did not significantly change after the improvement of the treatment technology. This means that the biological ammonium removal has no strong effect on the organic matter content of the source water.
Chapter IV: Evaluation of available water quality data and laboratory experiments

Fig 4.1. Fe, Mn, concentrations in the studied network before and after the new treatment technology

Fig 4.2. Ammonium concentrations in the studied network before and after the new treatment technology
Chapter IV : Evaluation of available water quality data and laboratory experiments

**Fig 4.3**: THM and ammonium concentrations in the studied water distribution network

![THM and ammonium concentrations graph](image)

**Fig 4.4**: COD\textsubscript{Mn} concentrations in the studied water distribution network

![COD\textsubscript{Mn} concentrations graph](image)

Figs.4.5 shows the increase of free chlorine (Cl\textsubscript{2}) and decrease of combined chlorine at the effluent of WTP after 2011, the date of starting the new treatment process.

Also it can be seen from Fig 4.6 and 4.7, the fast decay of free Cl\textsubscript{2} concentrations in different locations close to the input point of network, where rapid decay for Cl\textsubscript{2} was observed through the pipe network after the new treatment technology and its concentration reaches zero after short residence time.
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**Fig. 4.5**: Free and combined chlorine concentrations in the studied network before and after the new treatment technology

**Fig. 4.6**: Sampling locations in the water distribution network
Chapter IV: Evaluation of available water quality data and laboratory experiments

4.3 Results of Evaluation of water quality data

The biological ammonium removal technology had a considerable effect in reducing iron, manganese and ammonium concentrations in the treated water. The data evaluation showed decreasing in ammonium concentrations about 99% after the biological removal. As well, iron and manganese concentrations in the treated water had reduced about 96% and 94% respectively.

Although of the low level of iron, manganese and ammonium in the treated water (TW), it was observed that chlorine was consuming rapidly at the beginning of the distribution network. As well, the THM concentrations increased after applying the biological ammonium removal.

4.4 Results of laboratory experiments

The results of zeolite filtration which was applied on raw water samples at laboratory showed that ammonium concentration decreased about 96% after the zeolite filtration, while the decreasing was about 99% after applying the new treatment technology in water treatment plant. This result indicates that zeolite filter was able to reduce ammonium concentration in RW. Table.4.1 shows the values of temperature, Fe, Mn and dissolved oxygen (DO) concentrations in the raw water and after each kind of
treatment (after applying aeration). It can be seen that Fe and Mn concentrations were decreased after zeolite filtration by 70% and 32% respectively, while the decrease of these minerals after bio filtration in WTP was higher, about 96% for Fe and 94% for Mn.

The effect of bio-ammonium removal treatment on chlorine bulk decay is illustrated in Fig.4.8, it can be seen that the bulk chlorine degradation rate in the filtered sample (FW) was around the same in the bio-filtered one. As well, the chlorine demand of FW (70 %) was a little bit higher than demand of the bio-filtered sample (50%). These results can be attributed to the high concentration of manganese in the filtered sample (0.11 mg/L) comparing to the treated one (< 0.01 mg/L), besides to the remaining iron concentration (0.16 mg/L). However, in both samples, it can be seen that after 8 hours, the chlorine residuals were below the detection limit.

On the other hand, the effect of UV- irradiation disinfection on bulk chlorine decay was investigated. It was found that no considerable difference was observed in the chlorine decay curves between UV treated (TW) and non UV–treated (BUW) samples (Figs.4.9 and 4.10). In both samples, chlorine consumption through the first 1 hour was about 66% and 72% in case of initial chlorine doses 1.5 and 1.1 mg/L respectively.
Chapter IV: Evaluation of available water quality data and laboratory experiments

*Table 4.1. DO, ammonium, Fe, Mn concentrations in different water samples*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DO (mg/L)</th>
<th>T (°C)</th>
<th>Ammonium (mg/l)</th>
<th>Fe (mg/L)</th>
<th>Mn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water (RW)</td>
<td>8.0</td>
<td>17</td>
<td>1.08</td>
<td>0.56</td>
<td>0.16</td>
</tr>
<tr>
<td>Filtered water by zeolite (FW)</td>
<td>9.0</td>
<td>17</td>
<td>&lt; 0.01</td>
<td>0.16</td>
<td>0.11</td>
</tr>
<tr>
<td>Finished water after biological treatment (TW)</td>
<td>9.1</td>
<td>18</td>
<td>&lt; 0.01</td>
<td>&lt; 0.02</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

In the present work, the initial chlorine concentration (Co) was defined as the chlorine dose. During the experiments, it was observed that in case of high initial dosage (2 mg/L), the fast initial decay lasted for about 2 hours, and only for 30 min in case of lower dose (1.5 mg/L).

As already reported in previous literatures (Powell et al. 2000), it became apparent that if two identical samples were chlorinated with different initial chlorine concentrations (Co), the sample with the higher Co produced a lower decay rate. However, it was found that in all cases, chlorine decay decreased by increasing the initial chlorine concentration (Fig 4.11).

*Fig 4.9: Effect of UV-disinfection on bulk chlorine decay (Co=1.5 mg/l)*
Chapter IV: Evaluation of available water quality data and laboratory experiments

**Fig 4.10**: Effect of UV disinfection on bulk chlorine decay ($C_0=1.1 \text{ mg/L}$)

**Fig 4.11**: Bulk chlorine decay for different initial chlorine concentrations

The results of treatment by powder activated carbon (PAC) can be seen in Table 4.2. The turbidity of TW sample reduced from 0.07 NTU to less than 0.01 NTU, and the UV 254 absorption decreased significantly. In regards to COD$_{Mn}$ concentrations, they decreased by 76%, 70% and 30% after treatment with PAC, granular activated carbon (GAC) and coagulation respectively. However, the efficiency of PAC and GAC in
organic matter removal was similar, and the remaining \( \text{COD}_{\text{Mn}} \) concentrations were 0.48 - 0.56 mg/L in all samples after adsorption by PAC and GAC respectively.

*Table 4.2. NTU, UV\(_{254}\) and COD\(_{\text{Mn}}\) values before and after each treatment*

<table>
<thead>
<tr>
<th>Water source / Parameter</th>
<th>NTU</th>
<th>UV(_{254})</th>
<th>COD(_{\text{Mn}}) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water (RW)</td>
<td>0.94</td>
<td>0.07</td>
<td>2.2</td>
</tr>
<tr>
<td>Finished treated water (TW)</td>
<td>0.07</td>
<td>0.05</td>
<td>2</td>
</tr>
<tr>
<td>after powder activated carbon (PAC)</td>
<td>0.01</td>
<td>&lt; 0</td>
<td>0.48</td>
</tr>
<tr>
<td>after granular activated carbon (GAC)</td>
<td>0.02</td>
<td>NA</td>
<td>0.56</td>
</tr>
<tr>
<td>after iron salts (IW)</td>
<td>NA</td>
<td>NA</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The influence of organic materials on bulk chlorine decay was studied by performing multi experiments, before and after adsorption with PAC and GAC, for different chlorine doses. The results of these measurements showed that for the same chlorine dose, the bulk decay of PAC and GAC samples had decreased significantly comparing to TW samples as it is illustrated in Figs.4.12 and 4.13. The experiments showed decreasing the chlorine demand by reducing \( \text{COD}_{\text{Mn}} \) concentrations. In TW sample (\( \text{COD}_{\text{Mn}} = 2.0 \) mg/L, \( \text{Co} = 1.2 \) mg/L), the chlorine demand through the first 30 min was about 80% of the dose, while in the samples treated with PAC or GAC (\( \text{COD}_{\text{Mn}} = 0.48 \) and 0.56 mg/L respectively), the chlorine demand for the same period (30 min) was about 40% of the applied chlorine dose. In addition, the effect of initial chlorine concentration after decreasing the organic content was also studied. It was observed that increasing the chlorine dose from 1.0 to 1.2 mg/L resulted in decrease of the bulk decay rate and caused considerable increase in the residual chlorine concentration from 0.4 to 0.8 mg/L in the case of the same contact time (26 h) as it can be seen in Fig 4.14.

As well, varying the organic content in the water samples has affected significantly on the chlorine degradation as it is shown in Fig 4.15. Reducing \( \text{COD}_{\text{Mn}} \) 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). On the other hand, the chlorine decay in TW samples (\( \text{COD}_{\text{Mn}} = 2.0 \) mg/L) was very rapid and the chlorine demand was high (0.46 %) comparing to the chlorine
demand in the sample of COD_{Mn} = 0.8 mg/L, where it was about 0.13% for the same contact time (30 min).

These results confirm the effect of the organic components on chlorine consumption and correspond to the last result which showed increasing of THMs concentrations in the studied network since applying the bio filtration technology.

Ammonium removal from RW led to the presence of free chlorine in the system which reacts easily with natural organic matter in treated water, and generates disinfection by-products including THMs and AOXs. Recent studies of Water Works Company in the studied area (Czégény, 2014) showed significant increase in AOX and THM concentrations in the distribution network by increasing the chlorine doses, e.g. AOX concentration was about 185 μg/L at chlorine dose 2.0 mg/L. However, where iron, manganese and ammonium concentrations are at their minimum levels in the treated water (TW), it can be concluded that reactive organic species play a considerable role in the high and fast bulk chlorine decay and disinfection by-products (DBPs) are formed in the studied water supply system.

Fig 4.12: Bulk chlorine decay in TW, PAC and GAC samples for initial chlorine concentration (C_0) 1.2 mg/L
Chapter IV : Evaluation of available water quality data and laboratory experiments

**Fig 4.13** : Bulk chlorine decay in TW, PAC and GAC samples for initial chlorine concentration (Co) 1.0 mg/L

**Fig 4.14** : Bulk chlorine decay in PAC samples for different initial chlorine concentrations (1.0 and 1.2 mg/L)
Chapter IV : Evaluation of available water quality data and laboratory experiments

Fig 4.15: Bulk chlorine decay in water samples for different CODMn concentrations and initial chlorine concentrations (1.5 mg/L)

4.5 Summary and Conclusions

In this part of research, it can be concluded that reactive organic species plays a considerable role in the high and fast bulk chlorine decay and DBPs forming in water supply system, where iron, manganese, bromide and ammonium concentrations are at their minimum levels in the treated water (TW). Bio-filtration technology in WTP is effective in reducing ammonium level from raw water, and plays important role in THM formation by providing free chlorine in the network which reacts easily with organic compounds. Moreover, it can be seen that disinfection by UV irradiation has no important effect on chlorine bulk decay. The results of the experiments showed correlation between the bulk chlorine decay rate of treated water, the initial chlorine concentration and its NOM content.
Chapter V: Chorine Decay Modeling

**Bulk Chorine decay modeling**

5.1 Introduction

Chlorine decay behavior has been proved to be significantly affected by the components in the raw and treated water. Water treatment processes change the concentration of these components in the drinking water and are likely change the chlorine demand of water. Therefore, modeling of chlorine decay is important to find input parameters that can reflect the changes in water quality characteristics (Clark.R.M and Sivaganesan. 2002).

The objective of this part is definition an accurate kinetic model, which is able to describe the bulk chlorine decay. For this purpose, the kinetic models which previously detailed in chapter 2.4 was investigated for prediction the chlorine residuals.

Single and two-constituent decay models were applied on the collected data from laboratory experiments, and then tested to select the adequate model for bulk chlorine decay.

5.2 Kinetic models for bulk chlorine decay

Bulk chlorine decay is defined as reactions between the chlorine and chemical species in the water. The coefficients of bulk decay depend on the nature of the source water and the treatment it is received (Yeongho el at. 2010).

5.2.1 The experimental data

To investigate the kinetics of bulk chlorine decay, 152 of data were used. 124 data were used for models calibration and the left data for models validation. These data were divided into two sets of experimental data have been used:

1- The first data set was obtained by chlorination the effluent water 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. Table.5.1 shows the readings of chlorine residuals which were measured according to described methods in 3.8.2 and 3.8.3.
Table 5.1: Residual bulk chlorine for different initial chlorine concentrations and constant COD$_{Mn}$ : 2 mg/L

<table>
<thead>
<tr>
<th>Initial Dosing (mg/L)</th>
<th>3 (mg/L)</th>
<th>2.5 (mg/L)</th>
<th>2 (mg/L)</th>
<th>1.8 (mg/L)</th>
<th>1.5 (mg/L)</th>
<th>1.2 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hr)</td>
<td>Free Cl</td>
<td>Free Cl</td>
<td>Free Cl</td>
<td>Free Cl</td>
<td>Free Cl</td>
<td>Free Cl</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>2.5</td>
<td>2</td>
<td>1.8</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>2</td>
<td>1.5</td>
<td>1.2</td>
<td>0.8</td>
<td>0.7</td>
</tr>
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<td>1.8</td>
<td>1.8</td>
<td>1.4</td>
<td>0.9</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
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<td>1.7</td>
<td>1.2</td>
<td>0.7</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
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<td>1.5</td>
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<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
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<td>0.4</td>
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<td>0.2</td>
</tr>
<tr>
<td>8</td>
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<td>1.3</td>
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<td>0.1</td>
<td>nd</td>
</tr>
<tr>
<td>21</td>
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<td>0.8</td>
<td>0.4</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.8</td>
<td>0.7</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>0.6</td>
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<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
<td>2.5</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2- The second experimental data set was defined to investigate the effect of the organic content by dosing each diluted sample (section 3.9.4.D) 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. Tables 5.2 and 5.3 show the readings of residual chlorine concentrations in each sample with various COD$_{Mn}$ concentrations versus constant initial chlorine concentration (C$_o$) in each table.

Table 5.2: Bulk Chlorine decay for different COD$_{Mn}$ values and initial chlorine concentration (1.2) mg/L

<table>
<thead>
<tr>
<th>Cl$_2$ dose 1.2 mg/L</th>
<th>0.8 (mg/L)</th>
<th>0.96 (mg/L)</th>
<th>1.2 (mg/L)</th>
<th>1.44 (mg/L)</th>
<th>1.6 (mg/L)</th>
<th>2 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hr) / COD$_{Mn}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
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<td>1</td>
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<td>0.8</td>
<td>0.6</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.8</td>
<td>0.8</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.9</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>22</td>
<td>0.8</td>
<td>0.6</td>
<td>0.5</td>
<td>0.2</td>
<td>0.2</td>
<td>nd</td>
</tr>
<tr>
<td>24</td>
<td>0.8</td>
<td>0.5</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>0.7</td>
<td>0.5</td>
<td>0.4</td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter V: Chlorine Decay Modeling

Table 5.3: Bulk Chlorine decay for different COD_{Mn} values and initial chlorine concentration (1.5) mg/l

<table>
<thead>
<tr>
<th>Time (hr) / COD_{Mn}</th>
<th>0.8 (mg/L)</th>
<th>0.96 (mg/L)</th>
<th>1.2 (mg/L)</th>
<th>1.44 (mg/L)</th>
<th>1.6 (mg/L)</th>
<th>2.0 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>0.5</td>
<td>1.3</td>
<td>1.2</td>
<td>1.2</td>
<td>1</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>1</td>
<td>1.3</td>
<td>1.1</td>
<td>1</td>
<td>0.9</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
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<td>1</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>22</td>
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<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
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<td>nd</td>
</tr>
<tr>
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<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
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<td>nd</td>
</tr>
<tr>
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<td>nd</td>
</tr>
<tr>
<td>45</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

5.2.2 Single-constituent decay models

Firstly, simple analysis was performed to show the ability of single-constituent decay models (2.4.1) to express the behavior of chlorine decay in bulk water. For this purpose, the first set of experimental data was used for model evaluation (Table 5.1). First, nth, limited and parallel first-order models (Table 2.1) have been applied on the data to investigate the accurate prediction of chlorine residual for each model.

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 as shown by Eq. 5.1.

\[ SSE = \sum_{i=1}^{n} (y_i - f(x_i, y_i))^2 \]  

(5.1)

Where \( x_i, y_i \) the observed value and \( f(x_i, y_i) \) the predicted value.

The four kinetic models were compared according to the values of the determination coefficients (R^2) and the weighted error (\( \chi^2 \)) which was calculated as follow (Eq.5.2):

\[ \chi^2 = \sum_{i=1}^{n} \left( \frac{(y_i - f(x_i, y_i))}{\sigma} \right)^2 \]  

(5.2)

Where, \( \sigma \) is the estimated standard deviation. It was found out that the parallel first-order model gave the best fitting compared to other bulk kinetic models.
5.2.3 Comparison of single-constituent decay models

In general, 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. Figs 5.1 and 5.2 show that the shape of the parallel first order model fits the experimental data better than the other models. The figures illustrated the predicted bulk chlorine residuals concentrations according to each model in case two initial chlorine concentrations (1.2, 1.5 mg/L).

![Comparison of bulk chlorine decay models for Co=1.5 mg/L](image1)

**Fig.5.1.** Comparisons of bulk chlorine decay models for $Co=1.5$ mg/L

![Comparison of bulk chlorine decay models for Co=1.2 mg/L](image2)

**Fig.5.2.** Comparisons of bulk chlorine decay models for $Co=1.2$ mg/L

Table 5.4 appeared the determination coefficients ($R^2$) of the four kinetic models. The parallel first - order model provides higher values than the other models for different initial chlorine
Similar results were obtained concerning $x^2$ values. It was found that error values of the parallel first order were lower comparing to the $x^2$ of the remaining kinetic models.

**Table 5.4: The correlation values of the bulk chlorine decay models**

<table>
<thead>
<tr>
<th>Initial Dosing (mg/L)</th>
<th>First order model</th>
<th>Parallel first order model</th>
<th>nth order model</th>
<th>Limited model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$x^2$</td>
<td>$R^2$</td>
<td>$x^2$</td>
</tr>
<tr>
<td>3</td>
<td>0.23</td>
<td>8.50</td>
<td>0.98</td>
<td>0.14</td>
</tr>
<tr>
<td>2.5</td>
<td>0.64</td>
<td>3.57</td>
<td>0.99</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>0.86</td>
<td>1.42</td>
<td>0.99</td>
<td>0.09</td>
</tr>
<tr>
<td>1.8</td>
<td>0.67</td>
<td>2.28</td>
<td>0.99</td>
<td>0.002</td>
</tr>
<tr>
<td>1.5</td>
<td>0.89</td>
<td>0.73</td>
<td>0.96</td>
<td>0.03</td>
</tr>
<tr>
<td>1.2</td>
<td>0.65</td>
<td>2.12</td>
<td>0.95</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**5.2.4 Applying the parallel first-order model**

As described in section 2.7.1, the parallel first-order model assumes that the overall rate of chlorine decay can be divided into two phases of decaying processes: fast and slow components.

As it was found previously in section (5.2.3), applying the parallel first-order model on the first group of experimental data showed good fitting between the measured and predicted chlorine concentrations (Figs 5.1 and 5.2). Table 5.5 showed the values of the first estimation of the parallel first-order model coefficients.

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. All data of chlorine residuals were stored and categorized into 12 data groups according to their initial chlorine and COD$_{Mn}$ concentrations. The parallel first-order model equation (5.4) was allocated for each group as its fitting formula. Appointing the initial values and the boundaries of $k_1$, $k_2$ coefficients from 0 to $\infty$, and $x$ boundary from 0 to 1, the first estimation of the coefficients was performed for each data set (Table 5.5). 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. Figure 5.3 shows the fitting in case three different COD$_{Mn}$ concentrations (0.8,1.2 and 1.6 mg/L ).
Table 5.5: Coefficients estimation of the first data sets for different initial chlorine concentrations

<table>
<thead>
<tr>
<th>Initial Chlorine Dosing (mg/L)</th>
<th>Parallel first order model, COD_mn = 2 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
</tr>
<tr>
<td>3</td>
<td>0.03</td>
</tr>
<tr>
<td>2.5</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
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<td>0.23</td>
</tr>
<tr>
<td>1.2</td>
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</tbody>
</table>

Table 5.6: Coefficients estimation of the second data sets for different COD_mn Concentrations

<table>
<thead>
<tr>
<th>COD_mn Concentrations (mg/L)</th>
<th>Parallel first order model, Co = 1.2 mg/L</th>
<th>Parallel first order model, Co = 1.5 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
<td>$k_2$</td>
</tr>
<tr>
<td>0.8</td>
<td>0.008</td>
<td>2.1</td>
</tr>
<tr>
<td>0.96</td>
<td>0.02</td>
<td>2.14</td>
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<td>2.21</td>
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<td>2.87</td>
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</table>

Fig.5.3. Bulk chlorine decay according to the parallel first-order model in case three different COD_mn concentrations (0.8, 1.2 and 1.6 mg/l)
5.2.5 Two - constituent decay models

Two-constituent decay model (second - order model) was applied on the both sets of experimental data.

First, the second-order model (section 2.4.2) which was proposed by Clark (1998) had been tested on the first set of data (Table 5.1) to incorporate the effect of the initial chlorine concentration. Coefficients \((K, M)\) were determined by minimizing the sum of squared differences between chlorine concentrations measured during decay tests and the model estimates at corresponding times during simulation of these tests. Table 5.6 shows the parameter estimation with the second - order model for different chlorine dosing of one water sample taken from the effluent of the water treatment plant before chlorination. Figure 5.4 demonstrates the fitting of the first data set using the second- order model.

**Table 5.7: Coefficients estimation of the first data sets for different initial chlorine concentrations**

<table>
<thead>
<tr>
<th>Initial Chlorine Dosing (mg/L)</th>
<th>Second - order model, COD(_{in} = 2) mg/L</th>
<th>(K)</th>
<th>(M)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
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<td>0.74</td>
<td>0.75</td>
<td>0.91</td>
</tr>
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<td>0.74</td>
<td>0.28</td>
<td>0.94</td>
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<td>0.83</td>
<td>0.47</td>
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<td>0.96</td>
<td>1.69</td>
<td>0.99</td>
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<tr>
<td>1.2</td>
<td></td>
<td>0.85</td>
<td>1.5</td>
<td>0.99</td>
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</tbody>
</table>
Chapter V : Chlorine Decay Modeling

The second experimental data set had been selected to test the second order model in order to predict the residual chlorine concentration in case of changing the organic content of the water. The model coefficients \((K, M)\) were estimated by using MATLAB’s application (cftool). The fit for each run is constrained to have:

\[(K \geq 0), \ (M \geq 0)\]  \hfill (5.3)

The values of the estimated parameters via MATLAB software for different CODMn concentrations are shown in Table.5.7

Figure 5.5 shows the fitting between the experimental data and the predicted one with the second order-model for different CODMn concentrations (0.8, 1.2, 1.6 mg/L).

Table 5.8: Coefficients estimation of the second data sets for different CODMn Concentrations

<table>
<thead>
<tr>
<th>CODMn Concentrations (mg/L)</th>
<th>Second- order model , Co = 1.2 mg/L</th>
<th>Second- order model , Co = 1.5 mg/L</th>
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<tbody>
<tr>
<td></td>
<td>(K)</td>
<td>(M)</td>
</tr>
<tr>
<td>0.8</td>
<td>0.41</td>
<td>0.51</td>
</tr>
<tr>
<td>0.96</td>
<td>0.61</td>
<td>0.33</td>
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<tr>
<td>1.2</td>
<td>0.64</td>
<td>0.69</td>
</tr>
<tr>
<td>1.44</td>
<td>0.81</td>
<td>1.38</td>
</tr>
<tr>
<td>1.6</td>
<td>0.9</td>
<td>1.48</td>
</tr>
<tr>
<td>2</td>
<td>0.97</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Chapter V: Chlorine Decay Modeling

Fig. 5.5. Bulk chlorine decay according to the second-order model in case three different COD<sub>Mn</sub> concentrations (0.8 mg/l; 1.2 mg/l; 1.6 mg/l)

The second-order model appeared to have good capacity in prediction the residual chlorine. As can be seen from the figures (5.4 and 5.5), the second-order model represents an accurate prediction of chlorine residual for the selected data. It can be noticed from the first estimation of coefficients conducted with this model, that the estimated coefficients (K, M) are not independent from chlorine dosing and organic content.

5.3 Conclusions

In this chapter, it was proved that the parallel first-order model is more accurate than the other single-constituent decay models (First-order, n<sup>th</sup>-order, limited-order models). The parallel first-order model was therefore considered to predict properly the chlorine residual in water sample for different COD<sub>Mn</sub> concentrations.

Further, the initial analyses of the existing data obtained from chlorine decay experiments, showed that parallel first- and second-order models are properly able to describe the chlorine behaviour in the present system. The correlation coefficients of second-order model (R<sup>2</sup>) ranged between 0.72 and 0.99, while R<sup>2</sup> values were above 0.93. Moreover, it was found that the bulk decay coefficients of the parallel first- and second-order models are varying with two parameters mentioned earlier: initial chlorine concentration and organic content. The existence of possible correlation between these coefficients and those variables are evaluated in chapter VI.
Chapter VI : Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

Modeling the combined effect of initial chlorine concentration (Co) and COD\textsubscript{Mn} on the model coefficients

6.1 Introductions

Determination of decay coefficients by laboratory based testing is useful as a reference method, but is also time consuming, expensive, and impractical on a routine operational basis. Mathematical modeling of the relationships between decay coefficients and the factors affecting them would be of help in defining those coefficients in an expedited way and depends only on water quality data already collected in routine monitoring programs carried out by water works (Vieira et al., 2004).

As it was evident in chapter IV, the consumption of chlorine is influenced by both the raw water constituents and the subsequent treatment practices applied.

In this part of research, the defined models in chapter V (parallel first and second - order model) will be evaluated and developed by relating the model coefficients with different combinations of water quality parameters. After estimating the values of these coefficients as it discussed in sections 5.2.4 and 5.2.5, a second regression analysis was performed to determine these coefficients as functions of control variables Co and COD\textsubscript{Mn} depending on the results of the previous laboratory experiments.

6.2 Parallel first - order model coefficients

6.2.1 Variation of model coefficients with initial chlorine (Co) and COD\textsubscript{Mn}

As described in section 5.2.4, the parallel first order coefficients are varying with initial chlorine (Co) and COD\textsubscript{Mn} concentrations.

In order to describe the behavior of these coefficients as functions of the control variables (Co, COD\textsubscript{Mn}) , graphical approach has been used. Each coefficient (k\textsubscript{1}, k\textsubscript{2}, x), was plotted against each control variable in turn, while holding the other control variables roughly constant.

Figs 6.1 and 6.2 present a linear relationship between the parallel first- order model coefficients (k\textsubscript{1},k\textsubscript{2}) and the reciprocal of initial chlorine concentration (1/Co). It was
found that the determination coefficients ($R^2$) for both the rapid and slow decay coefficients were about 0.89, which shows a strong relationship between these variables. This finding agrees with those of Powell et al. (2000) and Al-Omari et al. (2004). On the other hand, it was observed that there is a clear increase in the fraction of chlorine, which reacts slowly ($x$) by increasing the initial chlorine concentration ($C_0$) as it is shown in Fig. 6.3. As a consequence, the fraction of chlorine rapidly reacting ($1-x$) decreased by increased $C_0$ concentration. $R^2$ value between $x$ and the initial chlorine concentration was about 0.67.

![Fig. 6.1. Relationship between $k_1$ and $1/C_0$](image1)

![Fig. 6.2. Relationship between $k_2$ and $1/C_0$](image2)
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

In regards to the influence of organic matter on parallel first-order model coefficients, it was observed that bulk chlorine decay coefficients have proportionally increased by increased CODMn concentrations. Figs. 6.4 and 6.5 illustrate an exponential relationship between each of the model coefficients ($k_1$, $k_2$) and CODMn. These observed relationships were stronger in case of $k_2$ ($R^2 = 0.91$) comparing to the correlations between $k_1$ and CODMn ($R^2 = 0.77$). This indicates the importance of reactions of organic compounds with chlorine in the fast phase of decay.

Concerning $x$, an inverse relationship was found between it and CODMn. For high CODMn concentrations, fraction of chlorine reacting slowly ($x$) was low, while the fraction reacting fastly ($1-x$) was high. As it can be seen from Fig.6.6, the correlation between CODMn and $x$ was good with $R^2 = 0.97$ in case of high initial chlorine concentration ($C_o = 1.5$ mg/l), and $R^2 = 0.95$ in case of low initial chlorine concentration ($C_o = 1.2$ mg/l).

$y = 0.2155x + 0.1278$
$R^2 = 0.67$

Fig. 6.3 Relationship between $x$ and $C_o$
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

**Fig. 6.4 Relationship between $k_1$ and $\text{COD}_{\text{Mn}}$**

- $y = 0.0011e^{2.6865x}$
- $R^2 = 0.91$

**Fig. 6.5 Relationship between $k_2$ and $\text{COD}_{\text{Mn}}$**

- $y = 4.6674e^{0.2496x}$
- $R^2 = 0.91$

**Fig. 6.6 Relationship between $x$ and $\text{COD}_{\text{Mn}}$**

- $y = -0.4856x + 1.1809$
- $R^2 = 0.95$

- $y = -0.2365x + 0.8783$
- $R^2 = 0.97$
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

6.2.2 Empirical equations

Depending on the previous correlations (section 6.2.1) that were observed among the coefficients of parallel first order model \((k_1, k_2, x)\), the initial chlorine concentration \((C_o)\) and \(\text{COD}_{Mn}\), functional equations for the bulk decay coefficients have been developed.

In this study, the bulk chlorine decay coefficients \((k_1, k_2)\) and fraction of chlorine \((x)\) have been modelled as follows (Eqs. (6.1), (6.2), (6.3)):

\[
\begin{align*}
  k_1 &= p_1 \ C_o^{(-m_1)} \ e^{n_1 \ \text{COD}} \\
  k_2 &= p_2 \ C_o^{(-m_2)} \ e^{n_2 \ \text{COD}} \\
  x &= d_1 \ C_o^{d_2} \ \text{COD}^{-d_3}
\end{align*}
\]  

Where \((p_1, p_2, m_1, m_2, n_1, n_2, d_1, d_2, d_3)\) are constants and should be estimated. 16 pair of data has been used. 12 pairs for estimating the previous constants and the remaining for verification the empirical equations. For constants estimating, the equations had been transformed into natural logarithms, and then Multiple Regression Analysis was run. The yielded equations:

\[
\begin{align*}
  k_1 &= 0.00057 \ C_o^{-3.2} \ e^{3.42 \ \text{COD}} \\
  k_2 &= 1.53 \ C_o^{-1.02} \ e^{0.44 \ \text{COD}} \\
  x &= 0.52 \ C_o^{0.71} \ \text{COD}^{-0.63}
\end{align*}
\]

Statistical measures such as \(R^2\) and RMSE (root-mean-square error) for assessment the correlation between predicted and measured data values were obtained. Table (6.1) showed the values of \(R^2\) and RMSE of the parallel first order model coefficients \((k_1, k_2\) and \(x)\).

Figure 6.7 and 6.8 show the fit between the observed and predicted \(k_1, k_2\) via the equations 6.4 and 6.5. It can be seen that there is a good correlation with determination coefficients: 0.94 and 0.86 respectively. On the other hand, the correlation between the observed and predicted \(x\) values according to the Eq 6.6 was tolerable \((R^2 = 0.59)\) compared to the other tested empirical equations. (Fig 6.9).
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

Fig 6.7: Predicted versus observed $k_1$ values

Fig 6.8: Predicted versus observed $k_2$ values

Fig 6.9: Predicted versus observed $x$ values
Chapter VI : Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

6.3 Second-order model coefficients

6.3.1 Variation of model coefficients with initial chlorine ($C_o$) and $COD_{Mn}$

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.

The influence of the initial chlorine concentration on these parameters ($K, M$) is reported in Figs.6.10 and 6.11. It was observed that there was an inverse correlation between $K$, $M$ and the initial chlorine concentration ($C_o$). $R^2$ value was 0.58 in case of $K$ and 0.89 in case of $M$. Here, it was found that the parameter of second-order model ($M$) significantly depends on the initial chlorine concentration ($C_o$).

On the other hand, according to Fig. 6.12 it seems that there is a proportional relationship between $COD_{Mn}$ and $K$ for two different $C_o$ concentrations (1.2, 1.5 mg/l). The determination coefficients were 0.84 and 0.95 respectively. A proportional relationship was also detected between $COD_{Mn}$ and $M$ with $R^2 = 0.78$, (Fig. 6.13). Therefore, it can be seen that $K$ and $M$ values increased by increasing $COD_{Mn}$ concentrations in water samples.

![Fig. 6.10: Relationship between $k$ and $Co$](image)

$y = 0.966x - 0.217$

$R^2 = 0.58$

$0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1 \quad 1.2$

$0 \quad 1 \quad 2 \quad 3 \quad 4$

$Co$ mg/l

$K$

67
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

Fig. 6.11: Relationship between $M$ and $Co$

\[ y = 4.3257x^{2.885} \]
\[ R^2 = 0.89 \]

Fig. 6.12: Relationship between $k$ and $COD_{Mn}$

\[ y = 0.5614x^{0.7962} \]
\[ R^2 = 0.78 \]

\[ y = 0.5624x^{0.7962} \]
\[ R^2 = 0.84 \]

\[ y = 0.4855x^{0.858} \]
\[ R^2 = 0.95 \]

Fig. 6.13: Relationship between $M$ and $COD_{Mn}$

\[ y = 0.8571x^{1.1596} \]
\[ R^2 = 0.78 \]

\[ y = 0.5614x^{1.6868} \]
\[ R^2 = 0.78 \]
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

6.3.2 Empirical equations

Two empirical relationships between \( C_{o}, \text{COD}_{Mn} \) and the second order model coefficients \((K, M)\) have been derived and compared. Equation (6.7) was utilized to model \( K \) and \( M \) mathematically as follow:

\[
K = a \cdot C_{o}^{b} \cdot \text{COD}^{c}, \quad M = d \cdot C_{o}^{e} \cdot \text{COD}^{h} \quad (6.7)
\]

Another functional relationship has been tested as can be seen in Eq 6.8:

\[
K = a \cdot e^{(b \cdot C_{o}) \cdot \text{COD}^{c}}, \quad M = d \cdot C_{o}^{f} \cdot e^{(h \cdot \text{COD})} \quad (6.8)
\]

Where \((a, b, c, d, f, h)\) are constants. To evaluate these constants, multivariate regression analysis was applied. Again, MATLAB software was used to estimate the constants of each functional relationship by non-linear regression.

After substituting the estimated values of constants in Eq 6.7 and 6.8, the yielded equations were:

\[
K = 0.58 \cdot C_{o}^{-0.26} \cdot \text{COD}^{0.76}, \quad M = 1.29 \cdot C_{o}^{-2.33} \cdot \text{COD}^{1.26} \quad (6.9)
\]

\[
K = 0.41 \cdot e^{(-0.17 \cdot C_{o}) \cdot \text{COD}^{0.5}}, \quad M = 9.8 \cdot C_{o}^{-3.13} \cdot e^{(1.2 \cdot \text{COD})} \quad (6.10)
\]

6.3.3 Performance of each empirical equation

Table 6.1 summarized the estimated values of constants with the determination coefficients \((R^2)\) and RMSE of the best fit between the predicted and observed values for each equation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Eq (6.9)</th>
<th>Eq (6.10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K )</td>
<td>0.84</td>
<td>0.79</td>
</tr>
<tr>
<td>( M )</td>
<td>0.82</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Eq.6.9 shows better fitting between the observed and calculated \( K \) values with \( R^2 = 0.84 \) and \( \text{RMSE} = 0.086 \) compared to Eq. 6.10 with \( R^2 = 0.79 \) and \( \text{RMSE} = 0.09 \). On the
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

Other hand, the relationship between the observed and calculated coefficient $M$ which obtained by Eq. 6.9 ($R^2 = 0.82$) was better than that yielded by Eq. 6.10 ($R^2 = 0.76$) and $RSME$ was 0.53 for Eq. 6.9, while it was 0.78 for Eq. 6.10.

Fig 6.14 shows that the observed $K$ values correlate well with the predicted values via equation 6.9, ($R^2 = 0.84$). The correlation between the observed $M$ values with the predicted ones via the same equation also appears to fit well with $R^2 = 0.81$ (Fig 6.15).

The functions of Eq. 6.9 are shown in Figs 6.16 and 6.17 respectively. Although the differences between the examined mathematical equations may often be slight, it could be suggested that the represented function in Eq. 6.9 is significantly better for describing the correlation between the coefficients of second-order model and each water quality parameter of the initial chlorine concentrations and $COD_{Mn}$. 

![Graph showing predicted versus observed K values via Eq (6.9)](image)
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

Fig 6.15: Predicted versus observed M values via Eq (6.9)

Fig 6.16: The functional relationship between CODMn, Co and K
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

Fig 6.17: The functional relationship between CODMn, Co and M

6.4 Validation of bulk chlorine decay models

Parallel first and second-order model for free chlorine residual decay was verified using independent data. 124 of experiments data were selected randomly and did not use for the model development.

6.4.1 Parallel first-order model

In order to test the ability of the parallel first-order model to predict bulk chlorine concentrations, Equations from 6.4 to 6.6 were used to calculate the parameters for Eq. 6.11, which represents the analytical solution of the parallel first order model. Then the predicted bulk chlorine concentrations were plotted versus the observed one as it can be seen in Fig.6.18

\[ C(t) = C_o \times e^{(-k_1 t)} + C_o (1 - x) e^{(-k_2 t)} \]  

(6.11)

It can be seen that the parallel first-order model achieved good fitting between the modelled and observed data with determination coefficient about 0.79.
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

6.4.2 Second-order model

The second-order model was also tested and applied to predict the bulk chlorine concentrations for the same set of data. After estimating $K$ and $M$ values via Eq (6.9), the yielded parameters were substituted into the equations 6.12 and 6.13 to calculate the free residual chlorine.

\[ u = M (1 - K) \]  \hspace{1cm} (6.12)

\[ C_A(t) = \frac{C_{A,0}(1 - K)}{1 - Ke^{-ut}} \]  \hspace{1cm} (6.13)

Then, the predicted residual chlorine concentrations were plotted against the observed ones (Fig. 6.19). It can be seen from the figure that the second-order model achieved good fitting between the modelled and observed data with determination coefficient of 0.83.
Chapter VI: Modeling the combined effect of initial chlorine concentration and organic matter on the model coefficients

6.5 Comparison of single-constituent (parallel first-order) and two-constituent decay models (second-order model)

The parallel first-order model and second order model provide good fitting between the measured and predicted data. Although the differences between parallel first- and second-order models may often be slight, it could be suggested that the second-order model is significantly better for describing chlorine decay, because it has better fit between the predicted and the observed bulk chlorine concentrations.

6.6 Results and Conclusions

The decay coefficients of both models were observed to show significant variation with the initial chlorine concentration ($C_0$) and organic content ($COD_{Mn}$), of water. To account for combined effects of $C_0$ and $COD_{Mn}$ on chlorine decay rate, empirical equations had been developed relating these parameters with coefficients of both parallel first- and second-order models. Two empirical equations have been derived for
mathematical modelling of the second-order model coefficients. It was found that equation 6.9 could significantly represent the correlation between these coefficients and these predictors ($C_o$, $\text{COD}_{\text{Mn}}$). Therefore, it was adopted to define the second-order model parameters ($K, M$) and to model the bulk chlorine decay.

It was also observed that the parameter of second order model ($M$) was dependent on the initial chlorine concentration $C_o$, and this result corresponds to the theoretical relationships of $M$ (Eq. 6.13) and confirms previous research results (Boccelli.et al. 2003).

Therefore, these equations could be used to update and improve the decay constants in water quality models. The relationship between chlorine decay parameters and water characteristics may be defined from experimental data and then can be used to predict decay parameters from periodical quality control performed on that same system.

As the result, it was clear that bulk chlorine decay coefficients depends on the quality of water, which is to be chlorinated.
Chapter VII : Conclusions and Recommendations

Conclusions and Recommendations

7.1 Conclusions

An initial study was conducted to investigate the effect of some selected treatment process and water quality parameters on bulk chlorine decay of effluent water from the drinking water treatment plant at a case study area. The decay of free chlorine was evaluated and modeled.

First, analyzing the available data of the studied network showed low concentrations of iron, manganese and ammonium in the treated water of the WTP effluent. Conversely, significant increasing in THM concentration after applying the biological ammonium removal technology was detected.

The research results showed that the biological ammonium removal is effective in reducing ammonium level from raw water, and plays important role in THM formation by providing free chlorine in the network which reacts easily with organic compounds. Some results concerning the biological ammonium removal and THM appearance in the water distribution systems have been collected from different waterworks, as it can be seen in Figs 7.1 and 7.2. Therefore, it is not only the results of the studied water supply system in this research.

Fig 7.1: THM concentrations after applying the biological ammonium removal in in the network of case study area No.1
Further, future measurements can be provided to show the concentrations of THM concentrations in treated water samples by the biological ammonium removal from the studied water treatment plant and in same samples but after treat them with activated carbon adsorption.

On the other hand, the pre-disinfection by UV irradiation has no significant effect on bulk decay and chlorine demand at the case study area, in contrast to the effect of PAC and GAC adsorption treatment. This result confirms earlier findings about the significant effect of organic content on chlorine degradation.

The experiments showed strong correlation between the bulk chlorine demand and decay rate of treated water and its NOM content (which was measured as COD$_{Mn}$). Reducing COD$_{Mn}$ concentrations led to significant decrease in chlorine consumptions.

The results of this study showed that the rate of bulk chlorine decay was affected by initial chlorine concentration and the organic content of the water.

In this work new methodology was adopted, by using COD$_{Mn}$ parameter in modeling of the bulk chlorine decay. This methodology could be appropriate for water utilities, where the equipment the total organic carbon (TOC) measurement is not available.
Chapter VII : Conclusions and Recommendations

During this research, several kinetic models for prediction of bulk chlorine decay were applied and compared. Among all discussed single-constituent decay models, the parallel first - order model satisfactory describes the chlorine decay behavior.

Further, the parallel first - and the second - order model were applied on two set of experimental data to simulate the bulk chlorine decay. Within the study, it was observed that the decay coefficients of both models were significantly varied with the initial chlorine concentration (Co) and COD_{Mn} of water. Therefore, empirical equations had been developed relating these two parameters with coefficients of both models (parallel first - and second - order model).

Through this research, it was found that the coefficient of second order model (M) was dependent of the initial chlorine concentration (Co), and this result corresponds to the theoretical relationships of M in Eq.2.19 and confirms results from previous research (Dominic.et al. 2003)

It was found that the parallel first- and second - order models show good fitting 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 was shown to perform better than parallel first order model. However, the magnitude of difference between the two model performances is dependent both on the water quality characteristics and the experimental conditions through chlorination.

7.2 Recommendations

To improve the disinfection efficiency in the water treatment plant (WTP) and to reduce the THM formation, process of organic matter removal in WTP should be studied consider.

On the other hand, the developed mathematical equations could be used to update and improve the decay coefficients in water quality models. The relationship between chlorine decay parameters and water characteristics may be defined from experimental
data and then can be used to predict decay parameters from periodical quality control performed on that same system.

7.3 Proposal for the practical application of the results:
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 can be applied an organic matter removal treatment in WTP by using granular activated carbon adsorption (GAC) before the chlorination.

The results of this work, in particular the equations of chlorine decay models of chlorine decay, are appropriate for the water utilities which measure the COD$_{Mn}$ as indicator for the organic content in water. However, these equations can be modified to reflect distribution system conditions.
Chapter VIII: The thesis

The new scientific theses

Thesis 8.1: biological ammonia removal

It was found that applying chlorination after the biological ammonia removal enhances by-products formation, especially THM formation. During the research, it was observed gradual increasing in THM concentrations in the studied water network since starting with the biological treatment in the studied water treatment plant. This could be attributed to the increase of free chlorine concentrations and the decrease of combined chlorine due to biological ammonia removal. Free chlorine can easily react with organic compounds in the water and form disinfection by-products (DBPs) compared to combined chlorine.

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.

As a result, it can be concluded that removing ammonium from raw water leads to provide free chlorine in the system which reacts easily with natural organic matter presented in treated water, and generates disinfection by-products including THMs. 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 8.2: 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 distilled 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, bromide
(which was measured by the water utility upon to our request) 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 8.3: simple methodology for modeling the bulk chlorine decay**

In this work new methodology was adopted, by considering COD\textsubscript{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\textsubscript{Mn}) as organic matter indicator of the water.

**Thesis 8.4: 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 (Co) and organic content (COD\textsubscript{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 ($R^2 = 0.79$).
Chapter VIII : The thesis

Thesis 8.5: 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 (Co), 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 CODMn and initial chlorine concentration (Co).

Publication list:

• Thesis 8.1:
DOI: 10.5593/SGEM2015/B52/S20.024

• Thesis 8.2:

• Thesis 8.3:
DOI: 10.3311/PPci.9273

• Thesis 8.4
DOI: 10.3311/PPci.9273

• Thesis 8.5

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  - J. Desalination 216. (1-3). 334–344.


Appendix

Appendix A1: Extended period simulation of the hydraulic model by EPANET

The hydraulic model was implemented in EPANET 2.0. Water consumption Patterns at the nodes were developed based on water flow measurements at the delivery point, which were obtained from the telemetry system, for a one month period (first to 30th January 2014).

An extended period simulation of 500 hours for the case study network was initiated. According to the type of pipes, Hazen-Williams coefficient (C) was determined to be (140) Pipe properties are listed in Table A.1

Table A.1: Length, size and type of the studied water supply pipes

<table>
<thead>
<tr>
<th>size (mm)</th>
<th>type</th>
<th>length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>PVC</td>
<td>844</td>
</tr>
<tr>
<td>90</td>
<td>PE</td>
<td>7630</td>
</tr>
<tr>
<td>100</td>
<td>PE</td>
<td>3203</td>
</tr>
<tr>
<td>140</td>
<td>PE</td>
<td>3113</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>23966</td>
</tr>
</tbody>
</table>

After the hydraulic simulation, the resulting flows at the network input are obtained and compared with the measured values.

Fig.A.1 appears the fit between flows at 23h. The results obtained by EPANET 2.0 simulators show a good calibration of the hydraulic model when comparing with the measured data.

Fig.A.1: Comparison between measured and simulated flows at network input
Appendix B1: Best fit curves for the chlorine decay according to the parallel first - order model in case different initial chlorine concentrations and COD$_{Mn}$ (2.0) mg/L (Temperature = 25 $^\circ$C)

\[ C_0 = 3.0 \text{ mg/l} \]

\[ C_0 = 2.5 \text{ mg/l} \]

\[ C_0 = 2.0 \text{ mg/l} \]


**$C_0 = 1.8$ mg/l**

- Modelled data
- Experimental data

---

**$C_0 = 1.5$ mg/l**

- Modelled data
- Experimental data

---

**$C_0 = 1.2$ mg/l**

- Modelled data
- Experimental data
Appendix B2: Best fit curves for the chlorine decay according to the parallel first-order model in case different COD$_{Mn}$ concentrations and initial chlorine concentration (1.5 mg/L) (Temperature = 25 °C)

![Graph showing chlorine decay curves for different COD$_{Mn}$ concentrations and initial chlorine concentration.](image)

- For $C_o = 1.5$ mg/l, the graph illustrates the comparison between modelled and experimental data for different COD$_{Mn}$ concentrations.
- The modelled data is represented by blue dots, and the experimental data is represented by orange dots.
- The graph shows the decay of chlorine concentration over time for different COD$_{Mn}$ values.

---

**Graph Details:*

- **$C_o = 1.5$ mg/l:**
  - Modelled data, COD$_{Mn}$ = 1.2 mg/l
  - Experimental data, COD$_{Mn}$ = 1.2 mg/l
  - Modelled data, COD$_{Mn}$ = 0.96 mg/l
  - Experimental data, COD$_{Mn}$ = 0.96 mg/l
  - Modelled data, COD$_{Mn}$ = 0.8 mg/l
  - Experimental data, COD$_{Mn}$ = 0.8 mg/l

- **$C_o = 1.5$ mg/l:**
  - Modelled data, COD$_{Mn}$ = 2.0 mg/l
  - Experimental data, COD$_{Mn}$ = 2.0 mg/l
  - Modelled data, COD$_{Mn}$ = 1.6 mg/l
  - Experimental data, COD$_{Mn}$ = 1.6 mg/l
  - Modelled data, COD$_{Mn}$ = 1.44 mg/l
  - Experimental data, COD$_{Mn}$ = 1.44 mg/l
Appendix C1: Best fit curves for the chlorine decay according to the second-order model in case different initial chlorine concentrations and COD$_{Mn}$ (2.0) mg/L (Temperature = 25 °C)

- $C_0 = 3.0$ mg/l
- $C_0 = 1.2$ mg/l
- $C_0 = 1.0$ mg/l
Appendix C.2: Best fit curves for the chlorine decay according to the second-order model in case different COD\textsubscript{Mn} concentrations and initial chlorine concentration (1.5 mg/L) (Temperature = 25 \degree C)

\begin{align*}
\text{\(C_0 = 1.5\) mg/l} \\
\text{modelled data CODmn =1.2 mg/l} & \quad \text{experimental data CODmn=1.2 mg/l} \\
\text{modelled data CODmn =0.96 mg/l} & \quad \text{experimental data CODmn=0.96 mg/l} \\
\text{modelled data, CODmn 0.8 mg/l} & \quad \text{experimental data CODmn=0.8 mg/l} \\
\text{\(C_0 = 1.5\) mg/l} \\
\text{modelled data CODmn =2.0 mg/l} & \quad \text{experimental data CODmn=2.0 mg/l} \\
\text{modelled data CODmn =1.6 mg/l} & \quad \text{experimental data CODmn=1.6 mg/l} \\
\text{modelled data CODmn =1.44 mg/l} & \quad \text{experimental data CODmn=1.44 mg/l}
\end{align*}