Influence of Water Quality Characters on Kinetics of Chlorine Bulk Decay in Water Distribution Systems

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Abstract

Several water quality parameters are contributing to the bulk chlorine degradation in drinking water system. The objective of this study is investigating the influence of the bio-filtration, initial chlorine concentration, UV disinfection and the natural organic matter (NOM) on the kinetics of bulk chlorine decay. Laboratory batch tests and various treatments including zeolite filtration, coagulation, powder (PAC) and granular activated carbon (GAC) adsorption were applied on different types of water samples. Results of this study indicated that bulk chlorine demand was high and its decay rate was rapid although of the low concentrations of iron, manganese and ammonium in the investigated samples. Disinfection by UV irradiation has no important effect on chlorine decay reverse to the influence of initial chlorine concentration and COD, where most of chlorine consummation was contributed mainly by NOM, and this result was supported by the observed increase of THM concentration in the studied network.

Keywords: Water quality, bulk chlorine decay, natural organic matter, UV disinfection

1. Introduction

Controlling free residual chlorine in water supply network is definitely important to ensure meeting required regulations and satisfying customer need. Chlorine disappears due to its reactions with ammonium, iron, manganese and organic compounds naturally present in different surface and subsurface water sources. In water distribution network chlorine also interacts with deposits and biomass at the inner pipes walls and with the pipe wall material (Wen et al.,1999). However, depending on the quality of water, types of treatment processes and the condition of distribution system, chlorine decay behavior is significantly variable. On the other hand, dosing too much chlorine has a number of negative effects, where high levels of chlorine raise the risk of forming disinfection by-products (DBPs) as trihalomethanes (THM) (Jae et al., 2012), which may be harmful to human health. Therefore, it is important to achieve a balance between the objectives of ensuring an adequate chlorine residual for microbiological quality and preventing high chlorine residuals that impact on the quality of the drinking water and may leads to health problems and consumer dissatisfaction. In Hungary, most significant quality problems of drinking water resources (Neunteufel & Laky., 2009) are the ammonium, iron, manganese and arsenic content. Presence of ammonium in the network may lead to form nitrite and nitrate ions and as well to decrease the efficiency of the disinfection provided by chlorine. This paper describes the influence of bio filtration (ammonium removal by microbiological nitrification), initial chlorine concentration, UV irradiation, natural organic matter on the bulk decay of free active chlorine.

The work was applied on real case study area located in Hajdú-Bihar County, at the east part of Hungary. Where several experiments had conducted at the laboratory on large number of water samples.

2. Literature Review

Previous studies have shown (Rossmanet al., 2001) the bulk chlorine decay as chlorine reaction with dissolved and suspended matter, mostly natural organic matter (NOM) in the water. Vieira et al., (2004) defined that the supplied water quality influences the rate of chlorine bulk decay (such as initial chlorine concentration, temperature, iron and the organic matter), while Hua et al., (1999) derived empirical formulae which describes the effects of temperature and the initial chlorine concentration on chlorine decay rate in different water samples. Hallam et al., (2002) also 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, and they concluded an inverse relationship between the bulk decay and an initial chlorine concentration. Chlorine will either decay due to reactions with compounds contained within the bulk water or due to reactions at the pipe wall. Powell et al., (2000) 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).In effect, chlorine reaction with the natural organic compounds contained in water leads to generate DBPs. The focus on the occurrence of DBPs in drinking water distribution systems has increased in the recent years. Special attention has been paid to the concentration of trihalomethanes (THMs: chloroform (CHCl3), bromodichloromethane (CHCl2Br), chlorodibromomethane (CHBr2Cl) and bromoform (CHBr3)) because of their potential carcinogenic effects (Rook., 1974) .

Chlorine decay and THM formation are determined by the dose of chlorineapplied, temperature, concentration and type of dissolved organic carbon (DOC) in water. DOC intreated water is influenced by the DOC concentration of source water and treatment processes applied for itsreduction. Past investigations have observed that the occurrence of THMs in chlorinated water may vary significantly according to season and geographical location in the distribution system (Williams et al., 1997).Some researchers have reported insignificant increases in DBP formation when pre- or post-UV irradiation is combined with existing chlorination method (Kashinkunti et al., 2004). On the other hand (Wei et al., 2012) found that UV irradiation alone and co-exposure to UV radiation and chlorine both influence the reactivity of NOM toward subsequent chlorination, and lead to similar increases in specific disinfection by-product formation potential (SDBPFPs) and total organic halogen formation potential (TOXFPs) in most trials. Some studies also showed that UV irradiation prior to chlorination of natural water did not affect the THM formation kinetics but chlorine demand was increased (Gallard & Von, 2002). However, the effect of UV irradiation on water quality depends on many factors, such as characteristics of source water quality, UV wavelength and the applied dosage (Yonkyu & Young., 2010). The goal of the current study is to investigate the effects of biofiltration treatment (microbiological nitrification of ammonium ions), UV irradiation and organic matter on chlorine decay and demand.

3. Materials and Methods

3.1 Studied Distribution Network

Fig.1 shows water supply network of a settlement in Hungary which is supplied by local water treatment plant. The water supply system consists of five wells (three of them are in operation) , new treatment plant (WTP), two reservoirs (100, 200 m^3) for the treated water, PVC and PE pipes with total length of 23 km and diameters range between 80-160 mm. The average daily consumption is 576 m^3/d and there is only one supply point of the network. The network was selected due to applying a new treatment process different than that was used 4 years ago, in correspond with executing a mechanical cleaning for pipes to eliminate the sediment and biofilm. The system was suffering from high iron, manganese and especially ammonium concentrations in raw water, which were leading to form the nitrite and nitrate in the distribution water pipes, in addition to decreasing the disinfection (by chlorination) efficiency. On November 2011, a new treatment process was applied on raw water to improve their quality and characters and to achieve effective removal for ammonium, iron and manganese. This advanced treatment involves respectively: aeration, fluidized bed filtration, UV disinfection, rapid sand filtration, disinfection by chlorine gas, two water storages and cartridge filter.

3-2 Analyzing the Available Data

Chemical, physical and microbiological data of water quality for the studied system have been collected at different locations by water utility from 2004 to 2013. These data were analyzed and checked, knowing that there were periods of missing and erroneous values for some parameters.

3.3 Kinetic Study and Tests

Chlorine reaction occurs both within the bulk water and with along the pipe wall. To determine the bulk reaction rate, a series of bottle tests have been conducted at the laboratory in the university. Water samples were collected from water treatment plant (WTP) at three points: raw water samples (RW) from wells, samples from the outlet of the Biofitration unit before UV disinfection (BUW), and finally, samples from the outlet of sand filters (treated finished water) before chlorination (TW). These samples transferred directly from the site to the laboratory of university to perform the tests. First, the temperature, pH and conductivity of the samples were measured, in addition to the concentration of Ammonium. To estimate the effect of the initial chlorine concentration on chlorine decay rate, several experiments were carried out at lab. Water samples dosed only with chlorine by using sodium hypochlorite solution (15000) mg/l after dilution to give varies chlorine concentration ranged from 0.8- 3 mg/l, and immediately after adding the chlorine, several vials (100) ml were filed with chlorinated water and closed tightly. The measurements performed at defined intervals and lasted until free chlorine concentrations reached 0.1 -0.2 mg/l. Before beginning any test, all containers were cleaned with de-ionized water and the free chlorine concentrations were measured on these sub-samples by using the (DPD) colorimetric method (Jaeet al., 2012). The color which developed was measured in pocket colorimeter (Nanocolor 400 D). Several experiments with de-ionized water were performed to control the tests.

To study the effect of biofiltration treatment on chlorine decay, raw water samples (RW) were treated at university lab by using natural zeolite filter. Zeolite has a mean diameter of 3–5 mm. The raw water was pumped slowly into the filter with influent pump to provide enough contact time and flowed upward through the zeolite layer, and then the effluent was collected in covered glass vessels. After filtration, ammonium, dissolved minerals (Fe, Mn) concentrations were measured in the filtered samples (FW). Later the samples were dosed with (1.0) mg/l of chlorine and compared to bio filtered chlorinated ones (BUW).In the treatment plant, UV irradiation is applied after fluidized bed filtration to kill organisms and bacteria. The influence of UV disinfection on bulk chlorine decay and demand was also studied in this research. Series of tests were carried out on BUW samples by adding different initial chlorine concentrations (1.1 -1.2- 1.5) mg/l, and compared to TW samples which also dosed with the same chlorine concentration. The effect of the natural organic matter (NOM) on bulk chlorine decay was investigated by performing different types of treatment in the laboratory to decrease the organic content in TW samples. First, 3.0 and 6.0 g of powdered activated carbon (PAC) were added to 500 and 1000 ml respectively of treated water (TW) to adsorb the organic compounds. Then the samples filtered by membrane filter (0.1 μm) to remove PAC.

The second method was by using granular activated carbon (GAC) adsorber. Zeolite layer was laid under granular activated carbon layer in a column, and then TW water was pumped to the GAC column with a pump to control the up inflow rate and to allow for longer contact time to eliminate the organic matter. Finally, two others finished water (TW) samples (300, 200) ml were coagulated by 2 and 6 ml of iron salts respectively and filtered through membrane filter (0.45 μm) to remove iron salts. All treated samples by PAC, GAC and coagulation were chlorinated with different doses ranged between 0.5 -1.8 mg/l, then chlorine concentrations in the samples were measured at defined intervals. The efficiency of the organic matter removal from the settlement water (TW) was checked by measuring the chemical oxygen demand (COD) for all samples by two methods. The first one was by using potassium dichromate ($K_2Cr_2O_7$, N 0.025), and the second was by using potassium permanganate ($KMnO_4$, N 0.01). UV absorption was measured also for each sample before and after treating with PAC. Ultra violet absorption at wave 256 nm (UV256) was conducted with a CARY 50 spectrophotometer, beside to measure the turbidity by electronic turbidity meter (430IR).

4. Results and Discussion

Analyzing of water utility data of the studied area shows clear decreasing in the concentrations of ammonium, iron and manganese in the finished treated water (TW) at different locations in the network after applying the new treatment process, see Fig.2.

On the other hand, it was observed increasing in THM concentration in the network year by year as shown in Fig.3, but at the same time, this increasing dose not exceeding the Hungarian Standard for THM limit (50 µg/ l).One of the reasons of this increasing may be attributed to existence of free chlorine in the system after applying the advanced treatment, where the combined chlorine (chloramine) was dominant before. Figs.4 and 5 show the appearance of free Cl2 concentration and decreasing of combined chlorine after 2011, the date of starting the new treatment. Further, it was observed that the residual chlorine decays rapidly after entering the distribution network through short travel time even after applying the new treatment technology and its concentration reachs to zero in locations, close to the input point of the pipe network Fig.6.

Effect of Biofiltration Treatment:

The values of temperature, dissolved oxygen (DO), ammonium, iron and manganese concentrations after filtration and treated water are showed in Table.1. It can be seen decreasing in Ammonium concentration after filtration RW by 96 %, while the decreasing was about 99 % after applying the new treatment technology. These results can indicate to the ability of the zeolite filter in reducing ammonium level in RW, in addition to the high efficiency of the applied treatment technology in WTP. On the other hand, iron and manganese concentrations decreased after zeolite filtration by 70% and 32% respectively, while the decreasing in TW was higher, about 96% for Fe and 94% for Mn. However, chlorine bulk demand and decay measurements are illustrated in fig.7, it can be seen that after dosing with 1.0 mg/l of chlorine, the free chlorine decreased quite fast in the filtered sample (FW) comparing to the biofiltered one (BUW). In addition, the chlorine demand of FW (70 %) was higher than BUW demand (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. However, in both samples, it can be seen that after 8 hours, the chlorine residuals disappeared.

Effect of Initial Chlorine Concentration

In all chlorine decay tests which applied on the treated water (TW), a fast initial decay was observed, this decay lasted for about 2 hours in the case of high initial dosage (2) mg/l, and for 30 min in case of lower one (1.5) mg/l, and then a second slow decay followed as shown in fig.8. In these tests the initial chlorine concentration was defined as the chlorine dose due to the high consumption of chlorine in the studied sample. However, as already reported in previous literatures (Powell et al., 2000), it became apparent that if two identical samples were chlorinated to different initial chlorine concentrations (Co), the sample with the higher dose produced a lower decay rate. In all case, it was found that decay rate is decreasing with increasing the initial concentration (Co).

Effect of UV Pre -Disinfection

Figs.9 (a) and 9 (b) illustrate chlorine degradation curves after adding two different chorine doses (1.1 and 1.5) mg/l to UV treated (TW) and non UV–treated (BUW) samples. As it can be seen, no considerable difference was observed in the demand and bulk decay rate between samples. Chlorine consumption through the first one hour was about 66% in the case of the high chlorine dose (1.5) mg/l and about 72% for the low dose (1.1) mg/l. However, the bulk chlorine decay rate in both samples was rapid and after 4 hours the free chlorine residual ranged between 0.1-0.2 mg/l in all samples. These results show that disinfection by UV irradiation has no significant influence on post-chlorination process. This observation differs from general expectation that UV disinfection can increase post-chlorine demand.

Effect of Organic Matter

The results of treatment by powder activated carbon (PAC) can be seen in table. 2. The turbidity values of TW sample reduced to less than 0.01 NTU, where the UV 256 absorption was less than zero and the COD decreased by 76%. On the other hand, the effect of treatment by granular activated carbon (GAC) was clear through reducing COD by 70%. The coagulation process with iron salts was not effective enough and the decreasing of COD was about 30% after coagulation. This means that most of the organic matter was removed by both powder and granular activated carbon treatment comparing to coagulation. Also the filtration treatment by zeolite did not occur any significant change in COD value and was inefficient to remove the organic compounds from raw water. However, the results showed that the efficiency of the activated powder and granular carbon in removal the NOM from TW was same, where COD values were approximately same (0.48 -0.55) mg/l in all samples after adsorption by PAC and GAC respectively. To investigate the impact of organic materials on bulk chlorine decay, multi experiments, before and after adsorption by PAC and GAC, are performed with different chlorine doses (1.0 and 1.2) mg/l.

The results of these measurements showed that for the same chlorine dose, the bulk decay rate of the PAC and GAC samples had decreased very significantly comparing to TW samples as it is illustrated in Fig.10 .It could be seen rapid chlorine decay rate, where the residual chlorine concentration was 0.1 mg/l after short travel time (3 hours) from dosing with 1.0 mg/l, while in both PAC and GAC samples, residual chlorine 0.1 mg/l could be obtained after travel time (24) hours. The experiments showed decreasing the chlorine demand after reducing COD. In TW sample (COD = 2 mg/l), the chlorine demand through the first 30 min was about 80% of the dose, while in the PAC and GAC samples (COD=0.48 and 0.56 mg/l) respectively, the chlorine demand for the same period (30 min) was about 40% of the dose. However, a significant correlation among chlorine dose, bulk chlorine demand and COD could be concluded. Decreasing COD from 2 mg/l to 0.48 mg/l at dosage 1.5 mg/l leads to decrease the chlorine demand by 60%.

The effect of initial chlorine concentration after minimizing the organic content also was so clear through the tests. Increasing chlorine dose from 1.0 to 1.2 mg/l yielded decreasing in the bulk decay rate and considerable increasing in the residual chlorine concentration from 0.1 to 0.6 mg/l for the same travel time 26 hours. These changes in chlorine decay and demand confirm the effect of NOM on chlorine degradation, especially where the concentrations of the ammonium, iron and manganese in the tested samples were so low. This could be imputed to rapid reactions occur between chlorine and high reactive organic material in TW which may lead later to form THM intermediates. Therefore, the treatment processes by granular and powder activated carbon may preferentially remove more NOM which has high specific chlorine demands. This result confirms 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 after applied bio filtration technology. Removing ammonium from RW led to provide free chlorine in the system whish reacts easily with natural organic matter presented in treated water, and generates by-products including THMs. Recent studies of Water Works Company in the studied area (Czégény, 2014) showed growing of AOX and THM concentrations in the distribution network by increasing the chlorine doses, where 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 plays a considerable role in the high and fast bulk chlorine decay and disinfection by-products (DBPs) forming in the studied water supply system .

Conclusions

In this research we can yield main conclusions:

- Although, the treated water (TW) at the outlet of water treatment plant (WTP) has a very low concentrations of iron, manganese and ammonium, the chlorine was consumed in fast way and the chlorine demand is high.
- The bulk chlorine degradation is characterized by two stages: rapid phase, where organic compounds are able to reacts fast with chlorine, and slow one due to slow reactions with the remaining chlorine.
- Biofitration technology in WTP has a considerable effectiveness in reducing ammonium level from raw water, but no effect was detected on chlorine degradation.
- The initial concentration of chlorine has a significant influence on chlorine bulk decay, and it is critical point to maintain residual levels of chlorine through water distribution system.
- The disinfection by UV irradiation has no important effect on chlorine bulk decay and demand, but on the other hand, it has high efficiency in killing microorganisms after biofiltraion treatments at the water treatment plant according to water utility data.
- The experiments showed an important correlation between the bulk chlorine demand and decay rate of treated water and its NOM content which measured as COD. Decreasing COD levels leads to reduce chlorine consumptions.
- PAC and GAC adsorption was found as an effective process in NOM removal in contrast to the coagulation. However, removal of organic compounds during treatment brings many benefits on disinfection process. Therefore the requirement for its adoption as a viable process in water treatment practice needs to study.
- Analyzing the available data of the studied network showed significant increasing in THM concentration, and these results correspond to the results of laboratory which enhance the effect of organic matter and free chlorine presence on chlorine decay and THM formation.
- To improve the disinfection efficiency, process of organic matter removal at WTP should be study, beside to study the ability of chancing the used disinfectant to another one that does not react with the organic materials (such as chlorine dioxide) should be taken in consider.

- Before designing the water treatment technology, laboratory tests should be performed in order to study the amount of organic matter in raw water. Strategies for minimizing THM formation while maintaining adequate free chlorine residuals in the water supply system should be evaluated.

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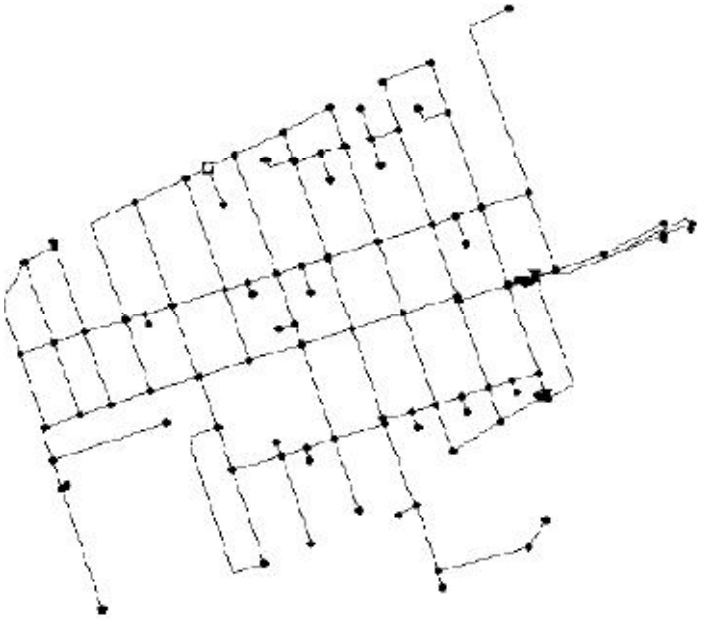


Fig.1: Water Distribution Network of the Studied Settlement

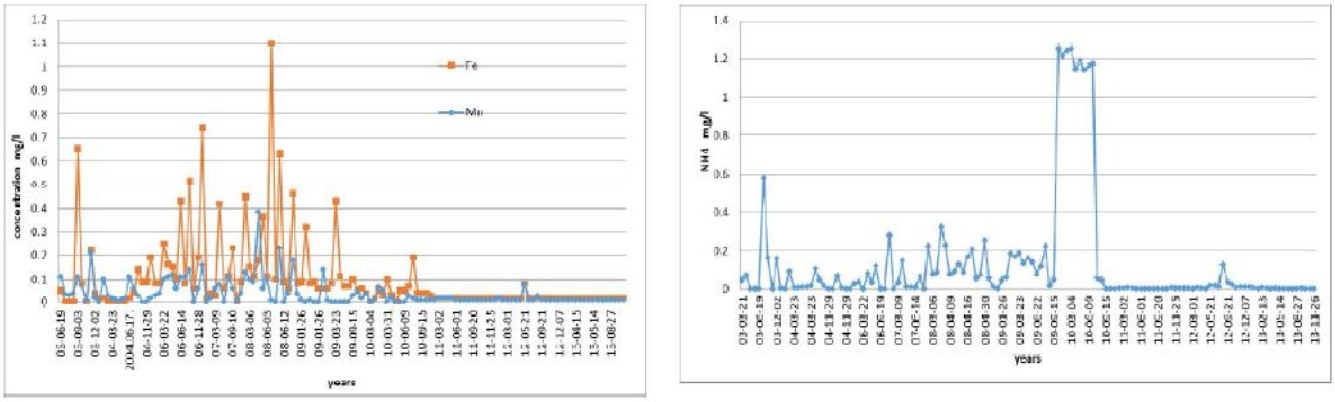


Fig. 2: Fe, Mn, NH4 Concentrations in the Studied Water Distribution Network before and after New Treatment Technology in 2011

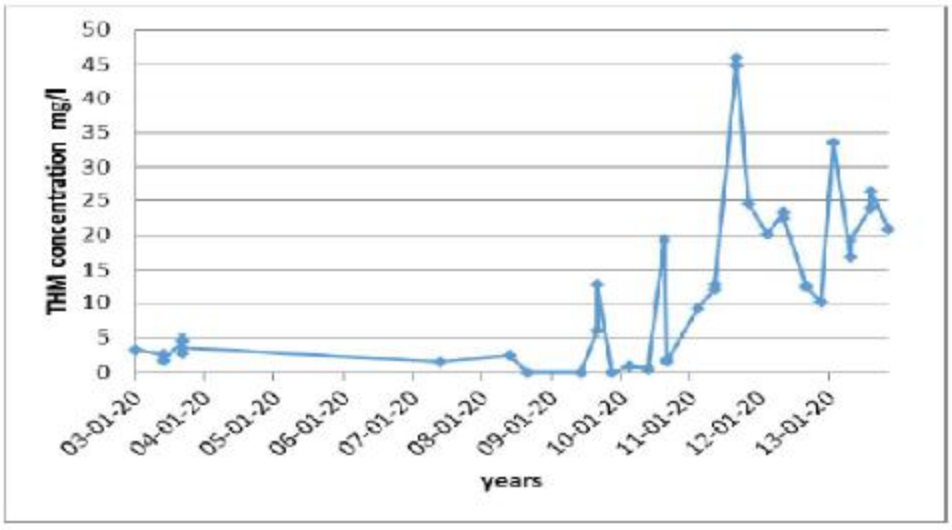


Fig.3: THM Concentration in the Water Distribution Network

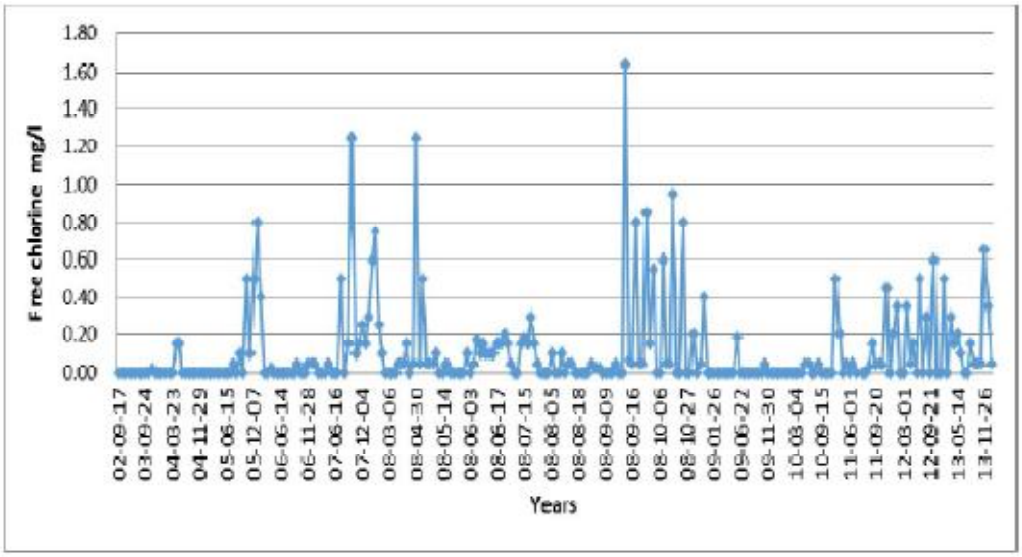


Fig.4: Free Cl2 Concentration in the Network

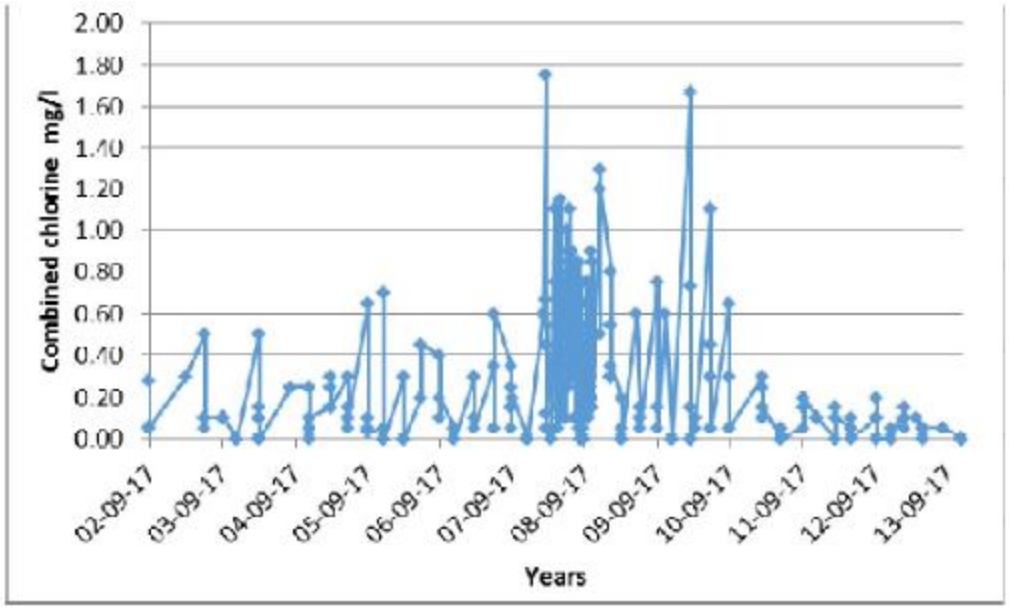
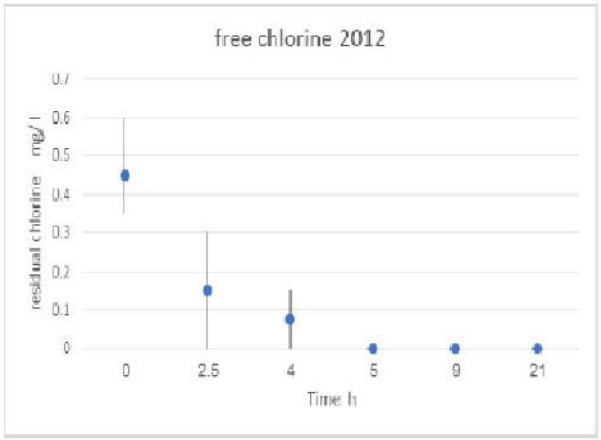


Fig.5: Combined Cl2 Concentration in the Network



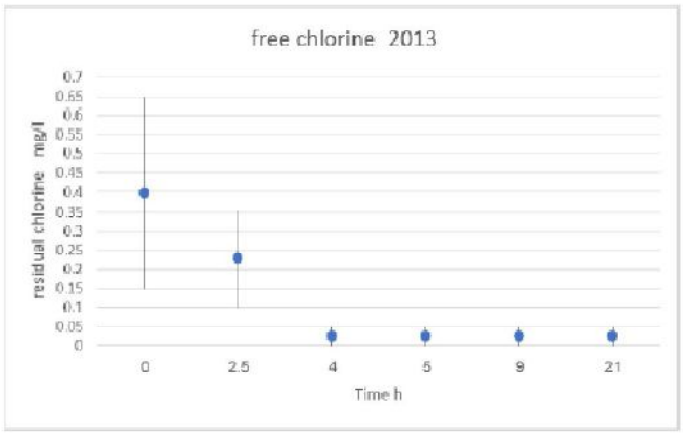


Fig. 6: Observed Free Chlorine Concentrations in the Water Distribution Network for Years 2012 , 2013

Table.1: DO, Fe, Mn and Ammonium Values

Parameter	DO (mg/l)	T (C°)	Ammonium	Fe (mg/l)	Mn (mg/l)
Raw water (after aeration) RW	8.0	17	1.085	0.56	0.16
Filtered water FW	9.0	17	0.032	0.16	0.11
Treated water TW	9.1	18	0.003	<0.02	<0.01

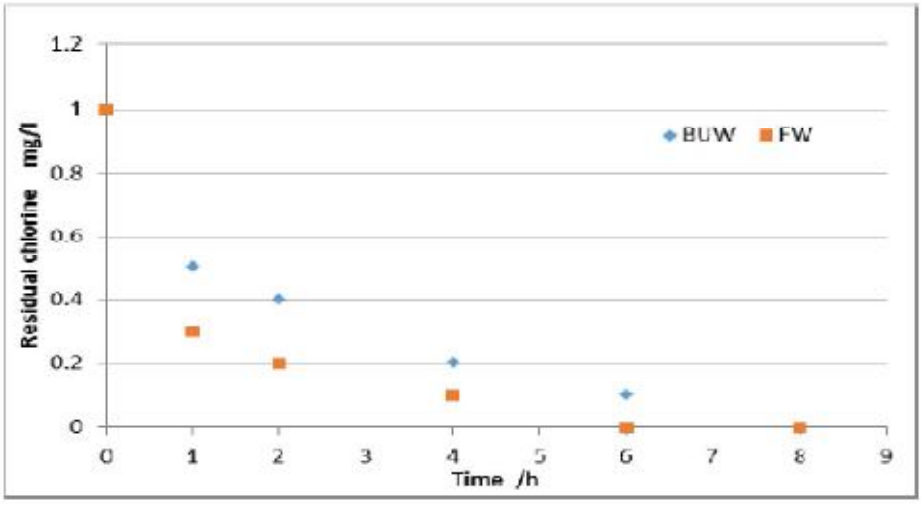


Fig. 7: comparing Chlorine Decay Kinetic after Zeolite Filtration and Biofiltration

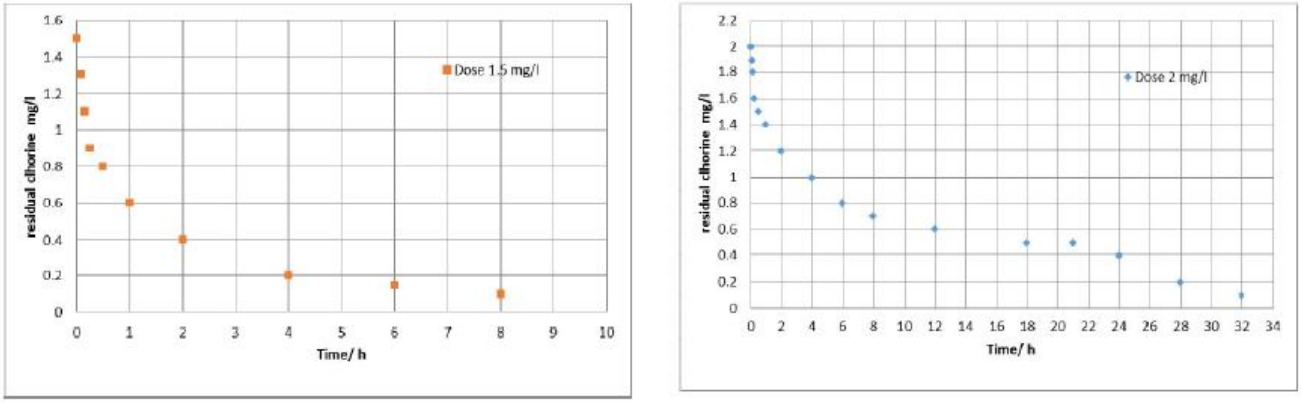


Fig. 8: bulk Chlorine Decay Results for Initial Chlorine Doses 1.5 and 2.0 mg/l

(a) *chorine dose : 1.1 mg/l* *(b) chorine dose :1.5 mg/l*

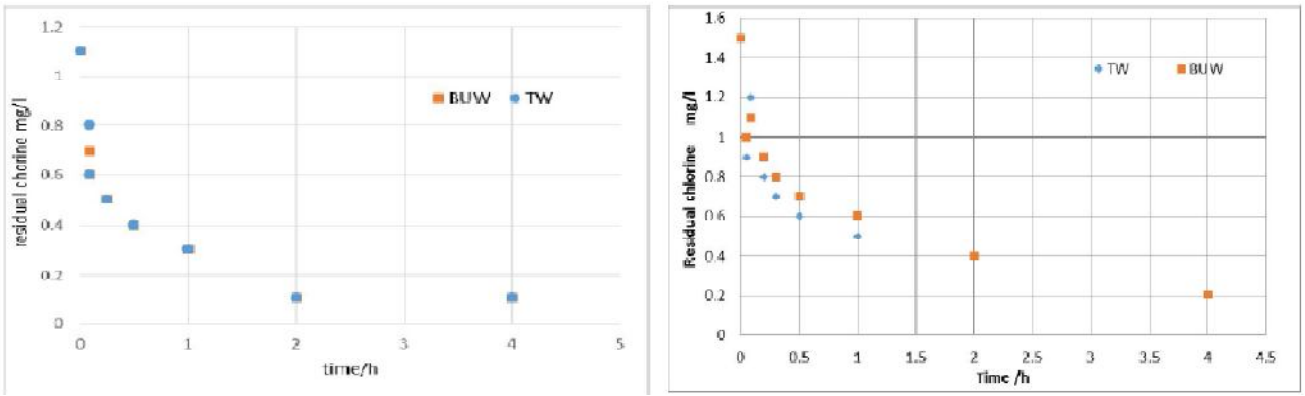


Fig.9: Effect of UV on Chlorine Decay

Table 2: NTU, UV256 and COD measurements

Parameter	NTU	UV 256	COD mg/l (KMnO4)	COD mg/l (K2Cr2O7)
RW	0.94	0.072	2.24	66.5
BUW	4.0	0.058	2.1	66.23
TW	0.07	0.046	2	56.5
PAC	<0.01	< 0	0.48	32.14
GAC	0.02	NA	0.56	NA
IW	NA	NA	1.4	NA
FW	NA	NA	2.2	NA

NA: not analyzed

(a)*Chlorine dose (1.0)mg/l* *(b) chlorine dose (1.2) mg/l*

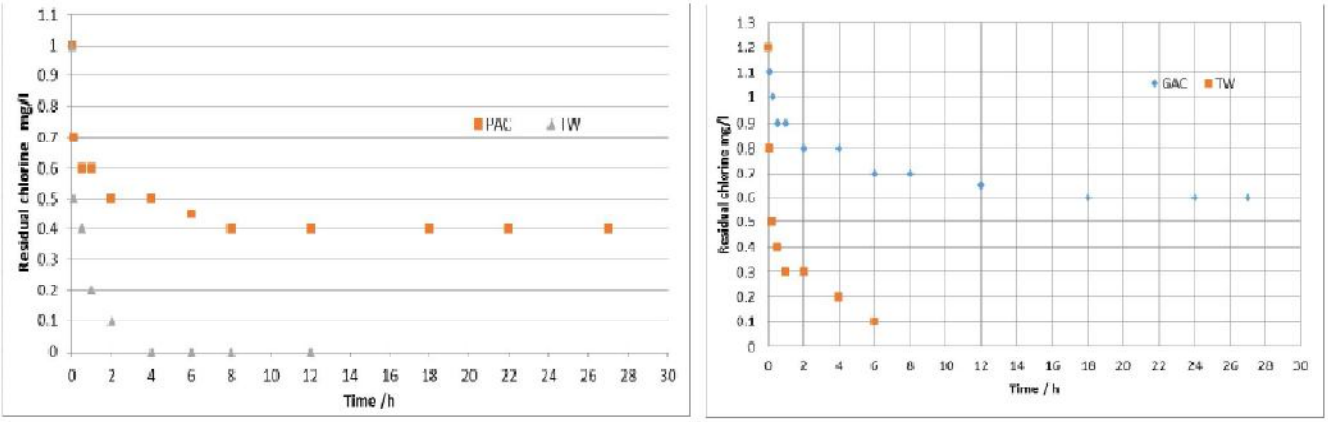


Fig 10: Chlorine Decay in TW, PAC and GAC