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Optimization of Breakpoint Chlorination Technologies for Drinking Water Treatment: a Hungarian Case Study

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Abstract

Ammonium ion is one of the major pollutants found in drinking water sources in Hungary, especially in deep aquifers. under oxidative conditions, ammonium can transform into nitrite ions in the water system, posing potential health risks. In Hungary mostly biological process or breakpoint chlorination are used to eliminate ammonium ion from raw water during the drinking water treatment process. When breakpoint chlorination is applied, harmful by-products are formed. Trihalomethanes concentrations have long been regulated in Hungary, therefore during the design and optimization of the breakpoint technologies trihalomethane concentrations have been considered. However, haloacetic acids (HAA5) and chlorate ion have been recently regulated in accordance with EU Directive 2020/2184. Chlorate is a by-product that appears in treated water when sodium hypochlorite is used in breakpoint chlorination.

Experiments were carried out at four Hungarian case study areas to determine the optimal strategy for breakpoint chlorination: applying higher chlorine dosages with lower contact times, or lower chlorine dosages with higher contact times. The investigations concluded that the preferable dosing strategy is to use lower chlorine concentrations and longer contact times. This approach reduces chemical demand (cost-effective) and has a neutral effect on THMs formation. it can be concluded that when the raw water contains ammonium ion concentrations above 0.5 mg/l, the use of sodium hypochlorite may raise concerns due to elevated chlorate ion levels in the treated water, particularly during summer. Further research is required to expand the optimization strategy, considering not only ammonium and trihalomethane concentrations but also chlorate concentrations.

Keywords

ammonium ion, breakpoint chlorination, by-products, chlorate ion, technology optimization

1 Introduction

Ammonium ion is a typical pollutant found in drinking water sources. In Hungary, it is present mostly in deep aquifers due to the geological environment. Bank filtration waters might also contain ammonium ions in elevated concentrations. It is not a typical pollutant in surface water sources, because in the presence of dissolved oxygen ammonium ion is converted to nitrite and then nitrate by the nitrifier bacteria. However, during winter, when the temperature does not favor the nitrification process, ammonium ions might appear in raw surface waters [1].

Moreover, anthropogenic activities can be another source of ammonium ions. In some places the discharge of inadequately treated wastewater that fails to meet regulatory requirements can contribute to the contamination of surface waters as well as groundwaters with inorganic constituents, including high concentrations of ammonium ions.

In Hungary, approximately 35% of drinking water originates from deep aquifers [2] which contain several pollutants of natural origin such as iron, manganese, arsenic, ammonium ion or methane gas [3]. The Drinking Water Quality Improvement Program in Hungary has actively supported projects aimed at removing ammonium ions. As a result, the majority of settlements now provide drinking water with ammonium ion concentrations below the parametric value of 0.5 mg/l (Fig. 1, [4]). This value is set by the Hungarian Government Decree No. 5/3023 (I.12.) in compliance with the European Directive 2020/2184.

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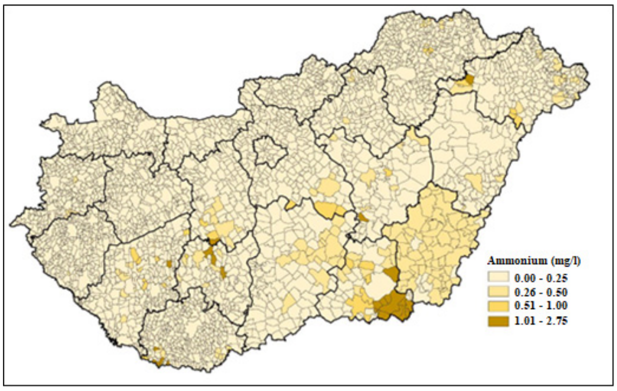

Fig. 1 Geographical location of settlements affected by ammonium ion in Hungary, 2021. [4]

Ammonium itself does not cause any harmful effects on human health. Nevertheless, it can become toxic when the exposure level exceeds 200 mg/kg body weight [5]. Additionally, under oxidative conditions in the water supply system, ammonium can be oxidized to nitrite ions. The critical situation arises when nitrite is not further converted to nitrate, and nitrite-rich water is supplied to the consumers.

Exposure to nitrite can cause methemoglobinemia, a condition characterized by an increase in methemoglobin levels resulting in reduced oxygen-carrying capacity of the blood which cause symptoms such as headache, fatigue and dizziness and in severe cases, blue baby syndrome (cyanosis) in infants. Furthermore, chronic exposure to nitrite has been linked to an increased risk of certain cancers including gastric, brain and esophageal cancer. It may also potentially harm the digestive, nervous, and reproductive systems [6, 7].

Furthermore, the reaction of ammonium ions with chlorine-based agents generates chloramine that has an unpleasant odor and causes a decrease in water disinfection effectiveness since it reduces the amount of disinfectant available to inactivate microorganisms [8].

Therefore, it is essential to eliminate ammonium ions from drinking water before it is pumped to water supply systems to ensure its health and safety for consumers, as well as to prevent the proliferation of certain bacteria in water distribution systems [9].

Numerous technologies have been employed in drinking water treatment plants for ammonium removal over the past few decades. These methods include ion exchange, adsorption, biological treatment, reverse osmosis, air stripping, and breakpoint chlorination [10–12]. Among these technologies mostly biological technology [13] or breakpoint chlorination is used in drinking water treatment plants in Hungary.

Breakpoint chlorination is characterized by a short and controlled contact time (minutes) with the use of large dose of chlorine, ranging from 1.0 to 10.0 mg Cl_2/l, resulting in residual free chlorine [14]. Due to the high chlorine dose used, this technology has a potential disadvantage which is the generation of harmful disinfection by-products (DBPs) in high concentrations, such as organic halogenides that include trihalomethanes (THMs), haloacetic acids (HAAs), haloketones, haloacetaldehydes, etc. [15, 14].

Chlorate is also an undesirable by-product that is formed if the chlorination process is carried out with sodium hypochlorite [16]. Exposure to chlorate can harm human health in different ways: it can impair the functioning of the thyroid gland by interfering with iodine absorption, which in turn leads to the nervous system and blood disorders, especially in young children, infants, and pregnant women. There is also some evidence that chlorate could have potential implications for cancer as well [17].

Hence, recently chlorate ion has been regulated in EU Directive 2020/2184 and also in the Hungarian Government Decree No. 5/2023 (I.12). Therefore, optimization of the breakpoint chlorination technology is crucial, in order to ensure that the DBPs are within acceptable levels of safety.

2 The application of breakpoint chlorination

2.1 The theory of breakpoint chlorination

Breakpoint chlorination is a widely used technique in water treatment to effectively eliminate ammonium ions by converting them into harmless nitrogen gas (N_2) [18]. Alongside with ammonium ions removal, other inorganic components present in the water can also be eliminated during this process. Particularly, low-valence metal ions such as iron (Fe^{2+}) and manganese (Mn^{2+}) are oxidized to form insoluble metal hydroxides that can be removed by sedimentation and filtration, resulting in improved aesthetic water quality. Although these side reactions consume some chlorine, the amount required is typically negligible, compared to that required for ammonium ion removal.

During breakpoint chlorination, a chlorine-based reagent typically chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) [19] are added to the water until a specific point, called the breakpoint, is reached.

During this process, a series of successive oxidative reactions occur in order to convert inorganic chloramines into nitrogen. Inorganic chloramines, also referred to as combined chlorines, comprise three species: monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine, or nitrogen trichloride (NCl_3). The ratio of their formation is mainly dependent on the molar ratio of chlorine to ammonia (Cl:N) and pH [20], while other factors such as the contact time and the temperature of the water have a lower effect [21, 22].

Several studies show that at acidic pH less than 4.4, trichloramine (NCl_3) is the predominant chloramine species in the water, whereas the optimal pH for dichloramine's ($NHCl_2$) formation ranges between 4 and 6, and high pH (7.5–9) resulted in the predominance of monochloramine (NH_2Cl) species [23, 24, 20].

When chlorine is added to the water an equilibrium between hypochlorous acid (HOCl) and hydrochloric acid (HCl) is established based on the following chemical reaction [25]:

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- . \quad (1)$$

At pH levels greater than 4, a substantial conversion of molecular chlorine occurs, leading to the formation of hypochlorous acid. An equilibrium is established between hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), where their distribution depends mainly on the pH and temperature of the water. At low pH and temperature, hypochlorous acid tends to be dominated and it reaches approximately 100% at pH levels equal to 6.

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

Hypochlorous acid reacts rapidly with ammonium ion or any compounds containing ammonium to form inorganic chloramines. At this first stage, where the chlorine to ammonia ratio (Cl:N) is low (less than 5), monochloramine (NH2Cl) is the predominant species which is a stable but weak disinfectant [26]:

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ . \quad (3)$$

With increasing chlorine addition, and at an intermediate chlorine-to-ammonia (between 5 and 10) monochloramine is converted into dichloramine, which imparts a distinct "swimming pool" taste and odor to the water [27, 18].

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad (4)$$

When the chlorine concentration and the chlorine-to-ammonia ratio are increased (above 10) [25], monochloramine and dichloramine, along with some chloroorganic compounds, are eliminated, resulting in the complete conversion of ammonium into trichloroamine (NCl_3).

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad (5)$$

The trichloro-amine compounds are unstable and decompose to nitrogen gas (N_2) which is volatile and escape from water.

$$HOCl + NCl_3 \rightarrow N_2 + HCl + Cl_2 \quad (6)$$

At this stage, the breakpoint is reached and it marks the complete disappearance of ammonia nitrogen, and indicates that the combined chlorine residual has reached its lowest possible level. Beyond this breakpoint, further addition of chlorine results in a steady increase in free residual chlorine (hypochlorite ion + hypochlorous acid) [18–28].

Consequently, water treated with chlorine will contain a mixture of free and combined chlorine, which is referred to as total chlorine. Theoretically, the mass ratio of chlorine and ammonium-nitrogen at the breakpoint is 7.6 [29, 18]. Nevertheless, it is important to note that this theoretical value may not accurately reflect reality as in practice the presence of the components in reduced form (e.g., Fe^{2+}, Mn^{2+}, H_2S, NO_2^-, natural organic matter) may necessitate higher chlorine dose.

Regarding the order in which chlorine reacts with different components in water (ammonium ions or the above-mentioned components), there are conflicting research findings in the literature. Some researchers mentioned that the reaction with ammonium ion is fast, therefore chlorine reacts firstly with ammonium ion [30]. According to Vernon and David [31] the rate constant of the reaction between chlorine and ammonium ion is 5.1×10^6 liter/mole-sec. And this reaction is first order with respect to both HOCI and NH3 and second order overall. In contrary, other researchers found that chlorine reacts first with the reducing agents [32].

2.2 The disinfection by-products of breakpoint chlorination

While breakpoint chlorination is effective in eliminating ammonium ions from drinking water, it also has a significant side effect. The high amount of residual free chlorine can react with both natural and anthropogenic organic and inorganic substances found in water, as well as bromide and iodide ions, leading to the formation of potentially harmful disinfection by-products (DBPs) at high concentrations [14, 15].

2.2.1 Organic by-products

Natural organic matters (NOM) are considered as the primary precursor for the production of DBPs [33] NOM is a heterogeneous and complex mixture of organic compounds that originates from biogeochemical processes such as aquatic organic matter decomposition and algal metabolic reactions. NOM can be classified into hydrophobic (fulvic acid and humic acid) that represent the major proportion, and hydrophilic compounds (carboxylic acids, amino acid, and carbohydrates) [34, 35].

In Hungary, where ammonium ion is critical mostly in deep wells, originating from geological conditions, the presence of NOM has significant effect on the formation is DBPs. The Great Hungarian Plain, known for its deep aquifers, notably contains a high concentration of natural organic matter. The complex composition of NOM poses challenges in understanding the precise mechanisms and the impact of various ions and metals on DBP formation [36]. Molecular weight, structure and hydrophobicity of NOM also affect the formation of DBPs.

Among the organic halogenated DBPs the following compounds are regulated in Hungary: trihalo methanes, haloacetic acids and there is a recommended limit for adsorbable organic halides.

- *Trihalomethanes (THMs)*

THMs precisely chloroform was first discovered by researchers from the US Environmental Protection Agency (EPA) and the Netherlands in 1974 [37]. They found out that THMs can cause serious health effects on humans and chloroform can even be carcinogenic. Since then, excessive studies have been carried out in order to corroborate the existence and health implications of THMs in potable water systems worldwide.

THMs consist of chloroform, bromoform, dibromochloromethane (DBCM), and bromodichloromethane (BDCM). According to the International Agency for Research and Cancer (IARC), THMs have different levels of carcinogenicity for humans. Chloroform, BDCM, and bromoform are classified as probable (B2) human carcinogens, meaning there is some evidence that they can cause cancer. DBCM is classified as a possible human carcinogen, based on an increased occurrence of liver cell tumors in male rats [38, 39].

Because of these health risks, THMs are regulated by several international and national authorities. The World Health Organization (WHO) has set a guideline value foreach of the THMs components which are 300 µg/l for chloroform, 100 µg/l for bromoform, 100 µg/l for dibromochloromethane (DBCM) and 60 µg/l for bromodichloromethane (BDCM), but it sets a limit of 100 µg/l for the total concentration of THMs in drinking water [40].

The European Union (EU) has adopted a directive that sets a maximum level of 100 µg/l for total THMs in drinking water, while the Hungarian regulation is stricter and allows only a maximum of 50 µg/l total THM concentration in drinking water (5/2023 Governmental Decree).

- *Haloacetic acids (HAAs)*

HAA9 includes monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), dibromochloroacetic acid (DBCAA), and bromodichloro acetic acid (BDCAA). At present, guideline values for only five HAAs are issued by the existing D/DBP rule, which is popularly known as HAA5 including MCAA, DCAA, TCAA, MBAA and DBAA (60 µg/l is the limit in EU Directive and also in the Hungarian regulation); whereas DCAA and TCAA are regulated by WHO [41, 42].

According to several studies, dichloroacetic acid (DCAA) and dibromoacetic acid (DBAA) have been found to cause adverse reproductive effects in mammals [43, 44]. They can also damage the liver, as indicated by toxicological reviews from the United States Environmental Protection Agency (US EPA). Moreover, DCAA has neurotoxic effects. Additional experiments conducted on rats have demonstrated that both DBAA and DCAA impair the fertility of adult male rats [45].

In addition, bromoacetic acid, DBAA, chloroacetic acid, and tribromoacetic acid are mutagenic in bacteria and to damage the genomic DNA of mammalian cells.

Three of the five regulated haloacetic acids (HAAs), which are dibromoacetic acid, dichloroacetic acid, and trichloroacetic acid, are carcinogenic and are classified as 2B Group of potential carcinogens according to IARC. They have the potential to induce various cancers, such as liver, leukemias and lung tumors.

- *Adsorbeable organic halides (AOX)*

AOX is a family of different organic compounds that contain chlorine, bromine, or iodine and can be adsorbed onto activated carbon [46, 47]. AOX can be formed from natural sources, such as humic substances, or from anthropogenic sources, such as industrial effluents, pesticides, or disinfection by-products.

AOX has various environmental and health impacts. They are bioaccumulative substances that can be toxic and some of them are carcinogenic. Some AOX compounds are also mutagenic and can damage the DNA of bacteria and mammalian cells. Additionally, they can damage the liver and kidney, cause eye and nerve irritation, and impair the reproductive system. For example, brominated or iodinated disinfection byproducts (DBPs) are highly cytotoxic and genotoxic [48, 49].

In conclusion, the parameter of adsorbable organic halides covers a wide range of substances, however neither the European Union, nor the World Health Organization regulate the maximum allowable AOX concentration in drinking water. In Hungary the Office of the Chief Medical Officer set a target value, which is maximum 50 µg/l, but the aim is to achieve less than 25 µg/l AOX concentration in drinking water.

- *Chlorate ion*

Significant percentage of the breakpoint technologies apply sodium hypochlorite instead of chlorine gas as it is easier and safer to handle. However, using sodium hypochlorite has a major drawback: it slowly decomposes to form chlorate, an undesirable byproduct [50].

The concentrated sodium hypochlorite solution is stored at the treatment plant for a while before it is added to the water. The appearance of chlorate highly depends on several environmental factors, such as temperature, time (length) of storage, the hypochlorite concentration of the solution, pH [51]. Vozik [52] studied the effect of storage time and temperature and it was found that chlorate ion concentration may be doubled within one month in summertime (in case of 2–4 g/l initial chlorate content).

The chlorate ion is formed based on the following two step reaction [16]:

$$\text{Step 1: } OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-, \tag{7}$$

$$\text{Step 2: } OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-. \tag{8}$$

The overall reaction can be written as follow:

$$3\ OCl^- + 3\ H_2O \rightarrow 2\ ClO_3^- + 3\ Cl^- + 6\ OH^-. \tag{9}$$

As a result of the above reactions, chlorate appears in the concentrated sodium hypochlorite solutions. When sodium hypochlorite is applied in order to remove ammonium ions, together with the active chlorine content chlorate ion is also dosed to the water. Because currently there is no cost-effective technology for the removal of chlorate ions from the water in subsequent treatment steps, it stays in the finished water.

Chlorate is considered a hazardous chemical that can have lethal health effects [53, 54]. Experiments in mice have shown that exposure to high chlorate concentration can cause methemoglobinemia which can result in hypoxia and in severe cases coma and death [55]. Based on some research results, chlorate can harm young children's neurological systems and induce anemia [54].

Chlorate can affect thyroid function by blocking the sodium iodide symporter (NIS) protein, which is responsible for regulating the amount of iodine in the thyroid. This could have possible consequences for both thyroid hyperplasia and cancer [56, 57]. However, due to insufficient toxicological data, chlorate is not classified by IARC.

Moreover, exposure to high amounts of chlorate can also cause respiratory effects, such as coughing, wheezing, and difficulty breathing [58].

The concentration of chlorate ion has been regulated recently both in EU (2020/2184 EU Directive) and at the national level (5/2023 Government Decree, Hungary), setting 0.25 mg/l as the maximum allowable chlorate concentration in the drinking water. Currently, several Hungarian water utilities face the chlorate problem, and they need to search for optimization strategies for their technology or to find another solution for ammonium ion removal (either by the application of chlorine gas or considering other ammonium ion removal processes, such as biological method) (Fig. 2).

3 The application of the breakpoint chlorination technology in Hungary

According to the Hungarian practice, chlorination (either in the form of chlorine gas or sodium hypochlorite) is applied not only as a final disinfectant, however, it is also used for pre or intermediate oxidation in order to convert ammonium ions to chloramines. This technology usually requires the use of chlorine doses that are an order of magnitude higher than the chlorine dose needed for post-chlorination, therefore chlorinated by-products might form in high concentration and granular activated carbon has to be installed in order to remove them. In case of unfavorable raw water quality (e.g., high organic content and high

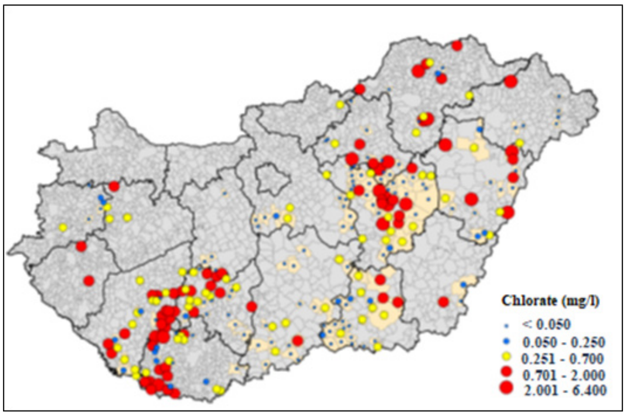

Fig. 2 Chlorate content of drinking water in Hungary [4]

ammonium concentration) it can be quite challenging to keep the THM concentration under the Hungarian limit (50 µg/l) in the finished water.

Breakpoint chlorination is often combined with iron, manganese, and arsenic removal, therefore often pre-oxidation with potassium permanganate is applied and coagulation is carried out with e.g., ferric salts in order to convert the soluble arsenic to particulate form.

In Hungary there are two typical configurations of breakpoint technology:

1. Chlorination is applied at the first part of the treatment (usually before the rapid filtration step) (Fig. 3).
2. Chlorination is applied right before the water is directed to the granular activated carbon (GAC). Granular activated carbon is a common treatment process that is used to adsorb undesirable components of raw water (i.e., micropollutants such as pesticides, herbicides, dissolved chemicals, particularly organic compounds and tastes and odours) in drinking water treatment plants [59] (Fig. 4).

Depending on the design some treatment plants apply contact tank as well in order to assure enough time for the breakpoint processes to take place. However, when no contact tank is utilized, the second configuration may pose challenges due to limited contact time for the breakpoint reactions. If the breakpoint chlorine dose is added to the water right before the water goes to the activated carbon adsorbents, it might happen that the contact time between chlorine and ammonium-rich water is too short and in order to achieve proper ammonium ion removal, therefore significantly higher chlorine dosages have to be applied.

The advantage of the first configuration is that longer contact time can be applied (even in the case when no special contact tank is used), because beside the hydraulic residence time in the water pipes, the breakpoint processes can take place while the water goes through the rapid filters. In this configuration usually lower breakpoint dosages can sufficiently remove the ammonium ions.

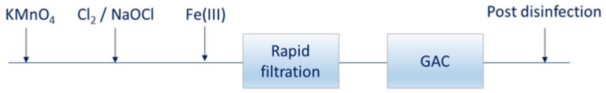

Fig. 3 Typical breakpoint chlorination treatment combined with iron, manganese and arsenic removal (breakpoint chlorine dose is applied at the beginning of the treatment process)

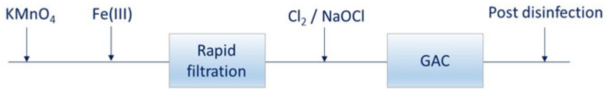

Fig. 4 Typical breakpoint chlorination treatment combined with iron, manganese and arsenic removal (breakpoint chlorine dose is applied before activated carbon adsorption)

There are special applications of breakpoint technology found in the literature such as a hybrid approach that integrates struvite crystallization and breakpoint chlorination [60], or the application of oxidative pre-treatment with the Fe(II)/Fe(III)-S(IV)-air system in order to reduce the concentration of organic contaminants (precursors) before breakpoint chlorination are applied [61].

4 Optimization of the breakpoint chlorination technology

4.1 Chlorine dose – contact time

When breakpoint chlorination is applied in practice operational parameters such as "chlorine demand" is often mentioned in order to describe how much chemical is needed in order to achieve proper ammonium ion removal efficiency. On the other hand, "contact time" is another important parameter, which shows how much time is needed for the breakpoint reactions to be completed. These two parameters are closely connected, despite that, they are often handled separately as two independent parameters.

In practice, the concept of chlorine demand is frequently discussed without taking into account the applied contact time. Similarly, the term contact time is often mentioned without considering the applied chlorine dose. However, it is important to recognize that these two parameters are not independent. Achieving the same level of ammonium ion removal efficiency can be accomplished by either applying a higher chemical dose with less contact time or using a lower chemical dose with a longer contact time.

Fig. 5 and Fig. 6 show a theoretical graph of how the surface describing the remaining ammonium ion concentration changes as the chlorine demand and contact time varies. If sections are made at different contact time values, the different curves show the remaining ammonium ion concentration as a function of chlorine dose for chosen contact time values (Fig. 5). When the sections are made at different chlorine dosages we get the reaction kinetic curves, which show the decrease of remaining ammonium ion concentration as a function of time for given chlorine dosages.

The question is which solution is better: applying higher chlorine dosages and lower contact times or lower chlorine dosages and higher contact times? When answering this question economic aspects have to be considered and besides that, the raw water characteristics have to be taken

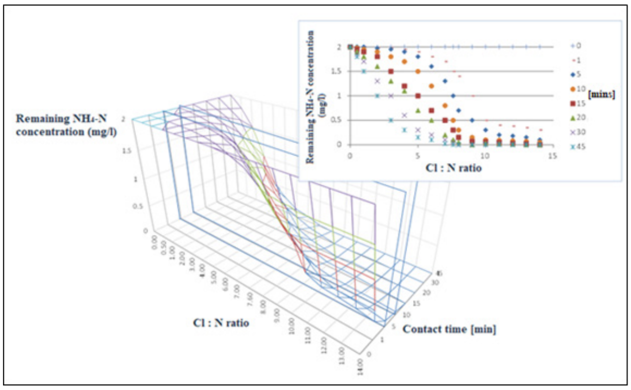

Fig. 5 Remaining ammonium ion concentration as a function of chlorine dose and contact time during the breakpoint process

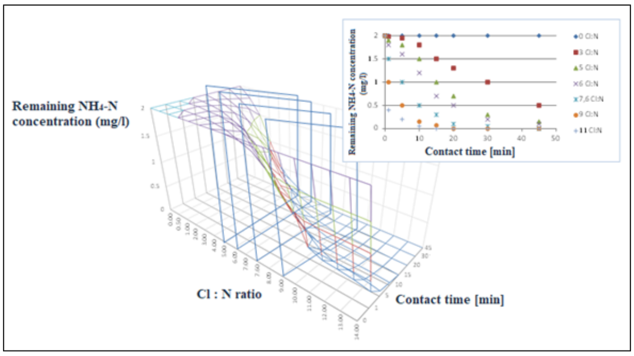

Fig. 6 Remaining ammonium ion concentration as a function of chlorine dose and contact time during the breakpoint process

into account and the concentration of by-products by the application of these two strategies has to be evaluated.

4.2 Optimization of the concentration of chlorinated organic by-products

4.2.1 Aim of the experiments

Experiments were carried out at four Hungarian case study areas in order to investigate, which strategy is better when breakpoint chlorination is applied: applying higher chlorine dosages and lower contact times or lower chlorine dosages and higher contact times. It is important to emphasize that HAAs and chlorate concentrations have been regulated only recently in Hungary (from January 2023), therefore in the experiments only the residual ammonium ions concentrations and THM concentrations were considered. During the optimization of the technologies, we were focusing on how to minimize the formation of THMs with changing the chlorine dosages and contact times. We were not dealing with the decrease of organic content before breakpoint chlorination or the optimization of GAC adsorption in order to minimize the THM concentration after breakpoint chlorination. We are aware that the complete technological optimization involves all these steps together with the "fine tuning" of water quality parameters such as pH, concentration of iron, etc., however we focused on the optimization of chlorine dose and contact time only.

4.2.2 Methods

Sodium hypochlorite solution was applied in the experiments, which was freshly diluted before each experiment. After dilution, the active chlorine concentration was measured before each experiment.

The experiments were carried out on-site with 500 ml of raw well water originating from deep aquifers. As a first step, the breakpoint curve was determined for each well water by increasing the chlorine dose with a fixed 30-minute contact time.

As a next step, experiments were carried out with the chlorine dose, which was found to be optimal at 30 minutes contact time and the applied contact time varied (from 2 minutes to 40 minutes).

In the third round of experiments, the chlorine dose was increased with 20–30%, and contact time was changed throughout the experiments (again from 2 minutes to 40 minutes). The aim of these experiments was to see how the needed contact time decreases by the elevation of the applied chlorine dose.

After adding chlorine (diluted sodium hypochlorite solution) to the water samples, mixing was applied and after the required contact time, ammonium ion, free active chlorine and total active chlorine concentrations were measured. For the reaction kinetic curves, where the breakpoint processes had to be stopped precisely, activated carbon powder was added to the samples after the required contact time, followed by filtering through 0.45 µm pore size membrane, and then ammonium ion concentration was measured from the filtrate. In those samples, where the concentration of organic by-products (trihalomethanes) was also measured, the breakpoint reactions were stopped with sodium thiosulphate solution (instead of activated carbon) after the required contact time. Activated carbon would adsorb THMs, that was the reason why in these samples sodium thiosulphate was applied to stop the breakpoint reactions.

The ammonium concentration, free active chlorine concentration and total active chlorine concentration were measured by spectrophotometric method with methods MSZ ISO 7150-1:1992 and MSZ 448-25:1981 (DPD method). Combined chlorine concentration was calculated as a difference between total active chlorine concentration and free active chlorine concentration. The trihalomethane concentration was measured by external laboratory with method MSZ 1484-5:1998, Section 7.3.

4.2.3 Results

Fig. 7 shows one of the breakpoint curves as an example (case study area No. 2). The optimal chlorine dose was found to be 8.5 (expressed in chlorine to nitrogen ratio), which is more than 10% higher than the theoretical breakpoint dose (7.6 Cl:N ratio). It is not surprising, because in practice higher chlorine dosages are needed than the theoretical value due to the presence of reduced compounds of the raw water (e.g., iron, organic material), which consume part of the chlorine.

The other breakpoint curves are not presented in this paper, however the Cl:N ratios are found in Table 1. In the third case study area, the needed chlorine dose was equal to the theoretical one, but in all other cases higher chlorine dosages were needed.

Table 1 also shows how the needed contact time decreases as the applied chlorine concentration increases at all case study areas. By increasing the chlorine dosages by 20–30%, the needed contact time decreased from 30 minutes to 10–15 minutes.

When the trihalomethane concentrations of the two strategies are compared it can be concluded that in these case study areas there is no difference between the two strategies: the same THMs concentrations were measured with the "low chlorine dose and high contact time" and "high chlorine dose and low contact time" strategy (Table 1).

However, this conclusion cannot be generalized based on these four case study areas. Carrying out experiments prior the treatment design is highly recommended in order to decide about the most effective plant configuration. If such pre-experiments are not carried out – and usually this is the case due to the lack of time – the design of two chlorine dosing point is recommended: one before rapid filtration and one before activated carbon adsorption. In this case the chlorine dosages can be optimized after the plant starts to operate and the decision can be done about how much chlorine has to be added at each dosing points.

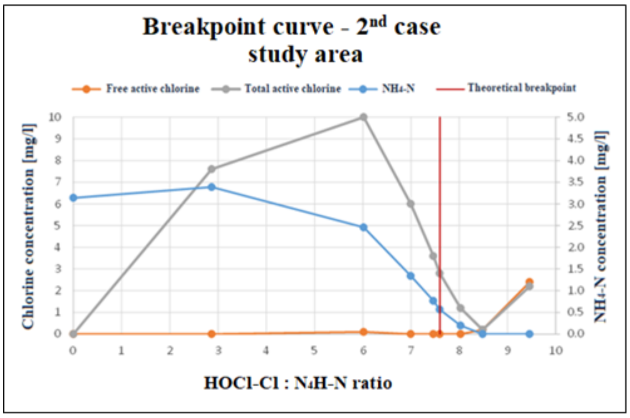

Fig. 7 Breakpoint curve at the second case study area (contact time: 30 minutes)

Table 1 Results of the experiments at the case study areas

Case study areas	NaOCl-Cl: NH4-N ratio	Contact time [min]	THM [ug/l]
1st case study area	8.5	30	Non detectable
	10.8	10	Non detectable
2nd case study area	8.5	30	20
	10.3	15	19
3rd case study area	7.6	30	2.9
	9.0	10	3.7
4th case study area	8.2	30	11
	9.1	10	11

5 The latest challenge – the chlorate issue

Due to the health concerns of chlorate ions when breakpoint chlorination is applied a third level of optimization is needed to be considered besides the ammonium removal and organic DPBs control: the concentration of chlorate ion has to be kept under the 0.25 mg/l limit in the treated water.

If we assume a linear increase of chlorate content in the concentrated sodium hypochlorite solution (90 g/l active chlorine content) from 2 g/l to 5 g/l and study different initial ammonium ion concentrations in the raw water (0.5 mg/l; 1.0 mg/l; 1.5 mg/l; 2.0 mg/l) with assuming 8.5 Cl:N ratio for ammonium ion removal, we found that the removal of 1 mg/l initial ammonium ion concentration can be already a problem, because above 3.5 g/l chlorate content of the concentrated NaOCl solution, the chlorate concentration of the treated water will be more than the 0.25 mg/l limit. The situation during practice is even worse because the active chlorine content of the NaOCl solution decreases as chlorate appears in the solution, therefore more chemical has to be added to the water, which results in even higher chlorate concentrations in the treated water (Fig. 8).

It can be concluded that the proper dosing strategy based on the investigations for the four case study areas is to apply lower chlorine concentrations and higher contact time, because:

- It decreases the chemical demand (which is cost effective);
- It has a neutral effect on the THM formation (it does not decrease, nor increases the THM concentration);

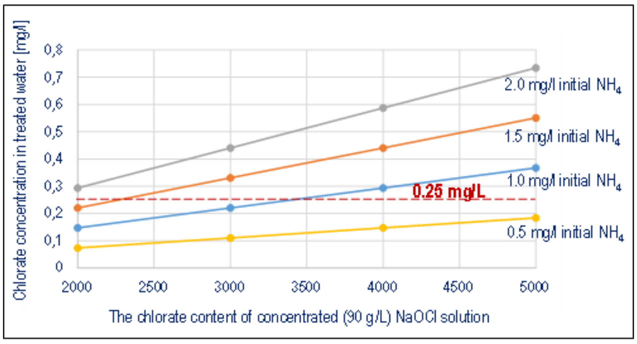

Fig. 8 The chlorate ion concentration in the treated water as a function of the chlorate content of the NaOCl solution and different initial ammonium ion concentrations

- By decreasing the chemical demand, the chlorate content of the dosed chemical will be also decreased (this last point is relevant only when chlorine is applied in the sodium hypochlorite form).

However, three out of the four case study areas have initial ammonium ion concentration more than 1 mg/l (the second case study area has extremely high ammonium ion content with more than 3 mg/l), therefore chlorate will be an issue at these three case study areas if NaOCl is applied for breakpoint chlorination even if such optimization is carried out. In such cases more drastic technological modifications are needed (e.g., applying chlorine gas instead of NaOCl solution or changing the ammonium ion removal technology to biological method).

When the experiments were carried out there was no limit yet for chlorate concentration in drinking water in Hungary, therefore during our research the problem of chlorinated organic by-products (namely THMs) were in focus. Since that time chlorate limit was introduced in Hungary as well, therefore in our future research we would like to deal with the chlorate issue and to investigate new optimization strategies for breakpoint chlorination technologies.

6 Conclusions

Breakpoint chlorination is a widely applied technology worldwide. In Hungary it is not used only for disinfection, however it is applied as an ammonium ion removal technology in drinking water treatment. When breakpoint technology is optimized for ammonium ion removal four aspects have to be considered:

- Proper ammonium ion removal efficiency has to be achieved;
- The amount of organic chlorinated by-products has to be minimized, meanwhile;
- The chlorate ion concentration has to be minimized (if sodium hypochlorite is used);
- Economic aspects.

The issue of chlorinated organic by-products has been investigated in several research works before, because the health effect of these compounds has been known for a long time, and there have been strict limits in the EU and national regulations. However, the chlorate problem has just came into focus recently. EU Directive 2020/2184 and the Hungarian Governmental Decree No. 5/2023 set 0.25 mg/l as maximum allowable chlorate concentration in drinking water, which is a huge challenge for those water utilities, which apply breakpoint chlorination with the application of sodium hypochlorite solution. Each affected water treatment facility has to be evaluated individually in order to see whether it is possible to optimize the breakpoint technology (and to achieve chlorate concentration less than 0.25 mg/l) by changing the chlorine dosages and contact times, changing the environmental factors, which have great impact on the appearance of chlorate ion in the concentrated sodium hypochlorite solutions (e.g. decreasing the temperature at the storage place). However, it has to be considered that the optimization has limitations if NaOCl solution is used for breakpoint chlorination, because above a certain initial ammonium ion level in the water and applied chlorine dose, we cannot avoid the appearance of chlorate above the limit in the treated water. If the required level of chlorate ion cannot be achieved by these measures more drastic technological modifications are needed: e.g., applying chlorine gas instead of sodium hypochlorite or switching to biological ammonium ion removal instead of breakpoint chlorination. Stefán et al. [62] have also suggested that the utilization of chlorine gas for the process of breakpoint chlorination represents a more favorable approach in terms of water safety. However, in order to achieve the best water quality each water supply should be individually studied.

After the preparation phase in future research, we are planning to focus on these optimization strategies with considering the economic aspects as well. We are in collaboration with Hungarian water utilities and our aim is to develop a technology selection guide based on a joint assessment of technical and economic aspects.

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