

Short thesis for the degree of doctor of philosophy (PhD)

Sulfur(IV) assisted oxidative removal of organic pollutants from source waters

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I. INTRODUCTION AND OBJECTIVES

In Hungary, 95 % of the raw water used in drinking water supply comes from groundwater aquifers, which are widely used due to the country's most favorable deep geological conditions. Thus, we take the accessibility of good quality drinking water for granted, as well as the fact that it is always available in sufficient quantities. Unfortunately, water pollution is a growing problem in many parts of the world, making it increasingly important and urgent to tackle it at the global and local level. There is a clear need for technological processes to reduce water supply and water quality problems, to prevent damage from so-called secondary sources of pollution in drinking water networks, and to purify water in an environment friendly way.

Depending on the quality of water and its intended use, there are different technologies for purifying deep water. A crucial and widespread technological step in these processes is the breakpoint chlorination, which is used to remove ammonia to comply with current legislation. One of the major environmental concerns of this treatment is the formation of various organic halogen compounds from organic constituents of raw waters. These disinfection by-products (DBPs) may not only be associated with taste and odor issues but may also have carcinogenic, teratogenic, or mutagenic properties.

The main objective of this PhD study is to explore how the Fe(II)/Fe(III)-S(IV)-air system can be utilized to reduce the chemical oxygen demand (COD) of raw waters used in the drinking water supply systems. In other words, how efficiently this oxidative pretreatment of raw waters can be used to remove organic contaminants which are the precursors of antagonistic halogenated species.

The principal concept of our approach is based on the fact that the catalytic auto-oxidation of sulfite ion in aqueous media produces reactive radicals that act as strong oxidants and eliminate the contaminants from the water.

Our further objective was to identify the optimum conditions for oxidative removal of COD. For this purpose, first it was systematically studied how the variation of the reactant concentrations and other experimental parameters affect the COD removal efficiency, and finally the Response Surface Methodology (RSM) was applied.

We also wanted to explore the impact of oxidative pretreatment on the formation of so-called trihalomethane derivatives (THMs) and adsorbable organic halogens (AOX) during the subsequent breakpoint chlorination.

Finally, our aim was to carry out microscopic biological and bacteriological studies to investigate the role of the oxidative treatment in the removal of microorganisms that may be present in raw water.

Essentially, our expectation was that the results would provide a firm basis for developing novel water treatment technologies to improve water quality and to prevent secondary water quality problems in the water production and distribution systems.

II. EXPERIMENTAL METHODS

The relevant properties of the raw waters included in this study are listed in Table 1.

Table 1. The relevant properties of the different raw waters

Sampling sites	COD (mg/L)	NH ₄ ⁺ (mg/L)	Fe (μg/L)	Mn (μg/L)	As (μg/L)	T (°C)	Total CH ₄ (L/m ³)
Apátfalva (Well III.)	5.08	1.39	75.8	16.1	3.09	22.1	4.46
Apátfalva (Well IV.)	6.91	1.19	106.6	149.4	1.90	19.7	7.77
Biharkeresztes (Well III.)	7.88	1.03	87.0	43.0	25.1	24	23.3
Földeák (Well III.)	2.70	1.58	151.1	22.6	21.9	31.1	2.47
Királyhegyes	7.02	1.11	97.5	22.1	7.70	18.5	7.16
Kismarja (Well II.)	7.02	0.71	138.0	78.0	< 0.5	13.8	-
Makó (Well. I-II-III.)	2.16	1.56	129.1	37.8	34.8	26.3	3.45
Nagyér (Well IV.)	3.20	0.20	774.0	161.0	25.1	14.8	1.7
Pocsaj (Well III.)	6.16	-	84.0	38.0	5.3	-	-
Pocsaj (Well IV.)	9.18	1.31	98.0	29.0	< 0.5	25.1	-

In a typical experiment, 250 mL raw water was added to a gas washing bottle equipped with a fritted disc. The steady gas flow was established by utilizing a Gilmont correlated laboratory shielded flowmeter (Thermo Scientific). Subsequently, Na₂SO₃, Fe₂(SO₄)₃, and FeSO₄ were added to the solution which led to the formation of a brownish precipitate.

After a sufficient contact time, samples were withdrawn from the reaction mixture, filtered with a 25 mm 0.45 μm Nylon Membrane syringe filter (VWR Syringe Filter), and analyzed for COD. The COD of the samples was determined by the standard KMnO_4 method. The main part of this study was made by using water from Királyhegyes, Hungary (EOV_y: 770635.8 m, EOV_x: 104066.9 m) which is characterized by relatively high COD (7.02 mg/L).

We have systematically studied how the efficiency of COD removal depends on the following parameters: total Fe concentration (c_{Fe}), relative concentration of Fe(II) ($Fe(II)\%$), sodium sulfite concentration ($c_{\text{S(IV)}}$), air introduction time, reaction time (t_{air}) and air flow rate (v_{air}).

It was verified by ion chromatography that the total amount of S(IV) in the treated samples was consumed. For the measurements, a Thermo Scientific Dionex ICS-5000+ ion chromatography system was used (guard column: Dionex IonPacTM AG19 RFICTM Guard 4 \times 50 mm, analytical column: Dionex IonPacTM AS19 RFICTM Analytical 4 \times 250 mm, detection: 250 nm, eluent: 20 mM NaOH, measurement time: 15 min, 25 μL loop-type injection).

The results from the systematic experiments were used as input to the response surface methodology (RSM) optimization procedure using the Design Expert[®] 11.0 (USA) RSM package. The robustness of the parameters was verified in control experiments by varying the predicted optimum reactant concentrations and reaction times by $\pm 20\%$.

The standard MSZ ISO 7150-1:1992 was used for the determination of ammonium ion in water. A color forming reagent (solution containing sodium salicylate, trisodium citrate and sodium nitroso-pentacyanoferrate(III)) and sodium dichloroisocyanurate solutions were added to the sample. The concentration of the ammonium ion was determined by

UV/VIS spectrophotometry based on the absorbance at the absorption maximum (655 nm) of the blue compound formed.

The raw waters were always dosed with the amount of hypochlorous acid required for breakpoint chlorination ($\text{HOCl} : \text{NH}_4^+$ mass ratio: 8.7 : 1), corresponding to a 100% sodium hypochlorite dose. After the addition of hypochlorous acid, the sample was stirred for one and a half hours. The process was stopped by adding sodium thiosulphate solution (3,5 g/L) and the concentration of ammonium ion in the treated water was measured.

The determinations of trihalomethane derivatives and AOX . was carried out in the accredited Central Laboratory of Debrecen Waterworks Ltd. The trihalomethane derivatives were measured according to MSZ 1484-5:1998, using a Thermo TRACE GC Ultra GC-ECD analyser equipped with an electron capture detector (ECD) and a RTX-624 30 m \times 0,32 mm \times 1,8 μm (Restek) and a ZB-SemiVolatiles 30 m \times 0,25 mm \times 0,25 μm (Zebron, Phenomenex) capillary column. The AOX content was analyzed according to ISO 9562:2004 standard using an ECS 1200 AOX, EOX, POX analyser (Thermo Fisher Scientific).

The bacteriological and microscopic biological tests were carried out according to European and Hungarian standards, both on water samples taken under sterile conditions and on water samples treated by oxidation. The *Coliform* count and the *Escherichia coli* count were determined according to MSZ EN ISO 9308-1:2015 and MSZ EN ISO 9308-1:2014/A1:2017, while the colony count of bacteria growing at 37°C and 22°C was determined according to MSZ EN ISO 6222:2000. Microscopic biological tests were determined according to ISO 448-36:1985. Samples were transported to the Central Laboratory of Debrecen Waterworks Ltd., stored at 4-8°C and processed within 24 hours.

III. NEW SCIENTIFIC RESULTS

3.1. *We have demonstrated that the oxidative method based on the Fe(II)/Fe(III)-S(IV) air system is suitable for reducing the chemical oxygen demand (COD) of raw water.*

3.1.1. In the raw waters used in this study, the organic substrates react with the strongly oxidizing radicals formed in the Fe(II)/Fe(III) catalysed autooxidation of S(IV) according to the scheme shown in Figure 1.

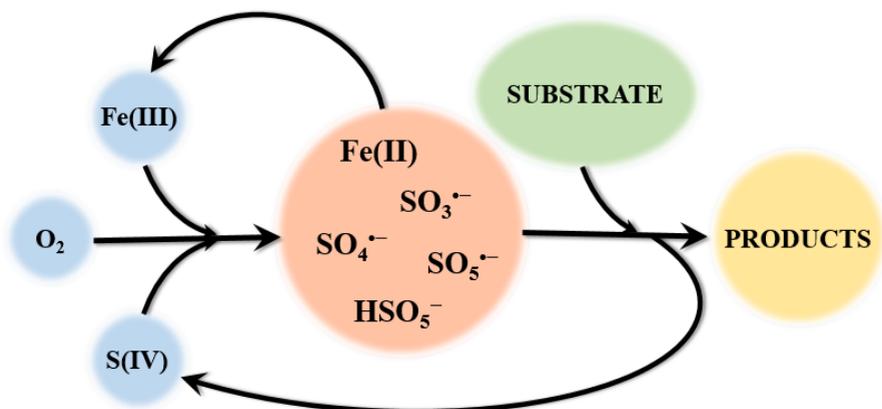


Figure 1. The oxidation of a substrate by utilizing the Fe(II)/Fe(III)-S(IV)-air system.

3.1.2. The efficiency of COD removal ($CODR\%$) by the Fe(II)/Fe(III) – S(IV) – air system greatly depends on the total concentration of Fe (C_{Fe}), the relative concentration of Fe(II) ($Fe(II)\%$), the concentration of sodium sulfite ($C_{S(IV)}$), the bubbling or reaction time (t_{air}) and the flow rate of air (v_{air}).

3.1.3. The effectiveness of COD removal reaches a limiting value by increasing the duration of bubbling air, but 100 % removal efficiency has never been achieved. The results confirm that some of the components contributing to COD cannot be fully oxidized by this oxidative method.

3.1.4. The efficiency of COD removal first increases and then sharply decreases as the flow rate is increased. This is the consequence of the interplay of the following effects. First, the reaction mixture becomes increasingly supersaturated with oxygen, and changes in the oxygen concentration fundamentally affect the rates of the competing reactions in favor of the oxidation of the substrate. On the other hand, air expels S(IV) from the reaction mixture at high flow rates. Regardless of the actual value of the other parameters, the optimum flow rate was around 200 mL/min, therefore this parameter was not changed in the subsequent experiments.

3.1.5. The efficiency of COD removal increases with increasing S(IV) concentration. A particular feature of the system is that no measurable decrease in COD is observed until the S(IV) concentration reaches a threshold value, which depends on the concentration of Fe(II) added ($Fe(II)\% = 100\%$) (Figure 2). Based on this observation, S(IV) should be used in relatively high concentrations. However, S(IV) is fully converted to sulfate ion, the concentration of which must not exceed 2.5 mM in the finished water according to the regulations in force (Joint Decree 6/2009 (IV. 14.) of the Ministry of Agriculture, Forestry, Environment and Water Management). This limit was observed in this work.

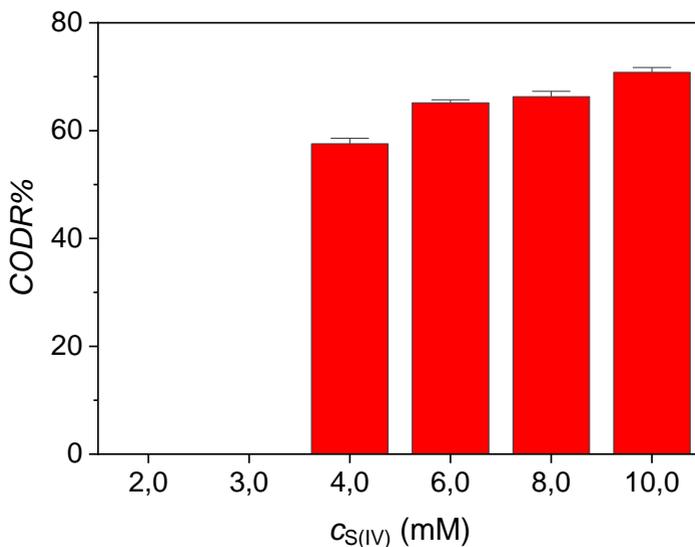


Figure 2. The removal efficiency of COD as a function of $c_{S(IV)}$.

$c_{Fe} = 4,0$ mM, $Fe(II)\% = 100$ %, $t_{\text{levegő}} = 60$ perc, $v_{\text{levegő}} = 200$ ml/perc.

3.1.6. The optimal total Fe(II) concentration (in the absence of initially added Fe(III)) is highly dependent on the total S(IV) concentration, i.e. the concentration ratio of these reactants also affects the efficiency of COD removal. As a first approximation, the observed trend can be interpreted by considering that a fraction of Fe(II) need to be oxidized to Fe(III) in the initial stage of the reaction to ascertain the catalytic cycle. Overall, this process also leads to the depletion of S(IV), which impairs the efficiency of COD removal. It is hypothesized that an optimal Fe(II)/Fe(III) concentration ratio must develop to make the oxidation of the organic contaminants dominant. At certain concentration ratios, the depletion of S(IV) is considerably faster than the oxidation of the substrate and the COD remains unchanged.

3.1.7. The efficiency of COD removal strongly depends on the ratio of Fe(II) to Fe(III) concentrations when the total concentration of c_{Fe} and S(IV) is constant. Increasing the relative concentration of Fe(III) is beneficial for a while, but counterproductive when the Fe(II):Fe(III) concentration ratio falls below a value that depends on other parameters.

3.1.8. At high total iron concentrations, catalytic autooxidation of sulfite ion becomes dominant, while the oxidation of organic components and the simultaneous regeneration of S(IV) are suppressed. The experiments clearly demonstrate that the efficiency of COD removal can be optimized by a suitable choice of reactant concentrations.

3.2. *We have determined the optimal conditions for maximum COD removal efficiency using the response surface method (RSM).*

3.2.1. To optimize the efficiency of COD removal, the compositions of the reaction mixtures used in the experiments were designed based on a three-level FC-CCD (*face centered-central composite design*) procedure. The parameter values were in the following ranges: c_{Fe} : 1.0-4.5 mM; Fe(II)\% : 0-100 %; $c_{\text{S(IV)}}$: 0.5-2.5 mM; t_{air} : 30-90 min and, based on the experimental results detailed above, the air flow rate was kept at 200 ml/min in all cases. In accordance with the previous discussion (Chapter 3.1.5.) the upper limit of $c_{\text{S(IV)}}$ was set to 2.5 mM. It has been verified that the four independent factors corresponding to these parameters (X_1 , X_2 , X_3 , X_4) should be coded at three levels between -1 and +1. Using the FC-CCD procedure, 21 experiments were performed. The experimental conditions and the resulting COD removal efficiencies are summarized in Table 2.

Table 2. The experimental conditions in accordance with FC-CCD and the corresponding reduction efficiency.

Run	c_{Fe} (mM)	$Fe(II)\%$	$c_{S(IV)}$ (mM)	t_{air} (min)	$CODR\%$ (%)
1	1.70	20	0.9	42	87.3
2	2.80	0	1.5	60	0.03
3	4.50	50	1.5	60	0.03
4	2.80	50	2.5	60	46.6
5	2.80	50	1.5	60	80.8
6	2.80	50	1.5	60	80.7
7	3.80	80	0.9	42	0.03
8	2.80	50	1.5	90	77.1
9	1.00	50	1.5	60	66.9
10	2.80	50	0.5	60	0.03
11	3.80	80	0.9	78	0.03
12	2.80	50	1.5	60	80.8
13	1.70	80	2.1	78	79.7
14	1.70	20	0.9	78	87.5
15	3.80	20	2.1	78	66.5
16	1.70	80	2.1	42	78.4
17	2.80	50	1.5	60	80.8
18	2.80	50	1.5	60	80.8
19	3.80	20	2.1	42	60.6
20	2.80	50	1.5	30	42.5
21	2.80	100	1.5	60	54.8

3.2.2. By randomly inserting five parallel measurements (experiments 5., 6., 12., 17. and 18.) into the experiment set, it was demonstrated that the COD removal efficiency is well reproducible (80.69 - 80.83 %).

The response parameter (COD removal efficiency) was fitted with the cubic approximation model (Equation 1).

$$\begin{aligned} Y = & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 \\ & + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + \\ & b_{123}X_1X_2X_3 + b_{234}X_2X_3X_4 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b_{112}X_1^2X_2 + b_{113} \\ & X_1^2X_3 + b_{114}X_1^2X_4 + b_{122}X_1X_2^2 + b_{133}X_1X_3^2 + b_{144}X_1X_4^2 + b_{223}X_2^2X_3 + \\ & b_{224}X_2^2X_4 + b_{233}X_2X_3^2 + b_{244}X_2X_4^2 + b_{334}X_3^2X_4 + b_{344}X_3X_4^2 + b_{111}X_1^3 \\ & + b_{222}X_2^3 + b_{333}X_3^3 + b_{444}X_4^3 \end{aligned} \quad (1)$$

Statistical analysis of the results showed that the F- and p-values of the parameters are significant. The coefficients R^2 (1.0000), the adjusted R^2 ($R^2_{\text{adj}} = 1.0000$) and the F-value of the model (3.621×10^5) confirm that the use of the cubic model is appropriate in this case.

3.2.3. The dependence of the predicted COD removal efficiency on the reagent concentrations was demonstrated using 3D response surface plots. As an example, Figure 3 shows the COD removal efficiency as a function of c_{Fe} and $c_{\text{S(IV)}}$. The RSM calculations demonstrate the complexity of the system.

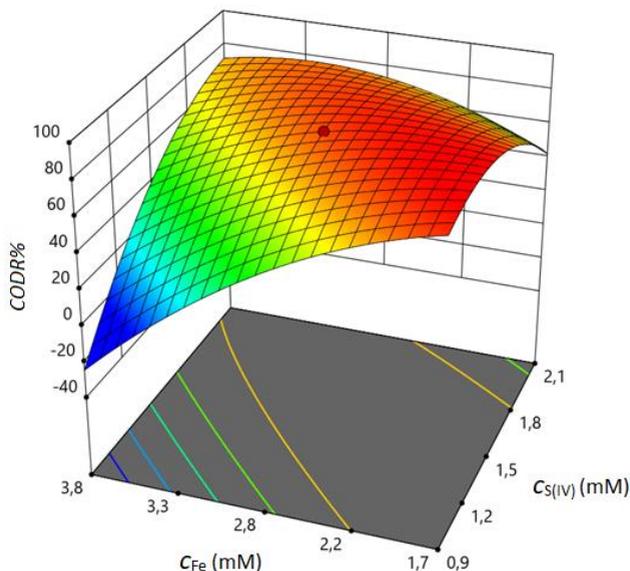


Figure 3. Response surface for COD removal efficiency as a function of total Fe and S(IV) concentration. $Fe(II)\% = 50\%$, $t_{air} = 60$ min, $v_{air} = 200$ mL/min.

As shown in Figure 4, the efficiency of COD removal varies non-monotonically with increasing C_{Fe} and $C_{S(IV)}$. The contour plot shows two favorable regions (red zones) at relatively low and high reactant concentrations. In the intermediate region (green zone), the efficiency of COD removal diminishes, suggesting that the oxidative depletion of S(IV) becomes dominant over the catalytic oxidation of the substrate. In agreement with the results in Table 2, no COD removal is expected at all in certain concentration ranges (blue zones).

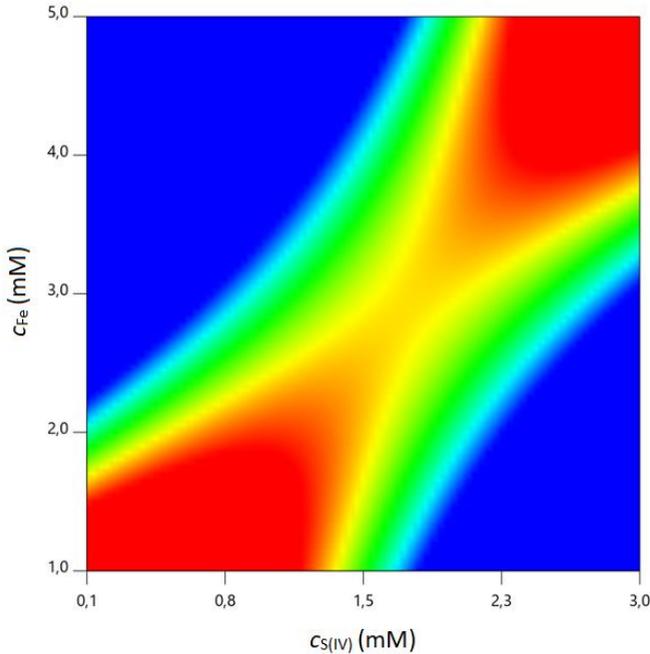


Figure 4. Contour plot of COD removal as a function of total Fe and S(IV) concentration.

The colors indicate the efficiency of reduction as follows, blue: 0 %, red: high (85.4 % at the optimum)

$$Fe(II)\% = 20 \%, t_{\text{air}} = 42 \text{ min}, v_{\text{air}} = 200 \text{ mL/min.}$$

3.2.4. The statistical procedure yields the following estimated optimized parameter values for the Királyhegyes raw water at 0.880 desirability level: $c_{\text{Fe}} = 1.7 \text{ mM}$, $Fe(II)\% = 20 \%$, $c_{\text{S(IV)}} = 0.9 \text{ mM}$ and $t_{\text{air}} = 42 \text{ min}$. Under these conditions, the measured and predicted COD removal efficiencies are $87.5 \pm 0.02 \%$ and 85.4% , respectively. This excellent agreement confirms the validity of the model.

3.2.5. The robustness of the COD removal efficiency was tested by varying the reactant concentrations by $\pm 20\%$ around the optimal values at the same reaction time (42 min). The results showed some variation, but the efficiency of COD removal was never less than 75.4%.

3.3. *We have demonstrated that the oxidative method presented here is generally applicable for the removal of significant levels of COD from various raw waters used in the drinking water supply.*

3.3.1. To prove the general applicability of the Fe(II)/Fe(III)-S(IV) air oxidation method, the efficiency of COD removal in raw waters from different locations was investigated using the optimum parameter values established for the Királyhegyes raw water. The removal efficiency varied from $62.0 \pm 0.01\%$ to $88.5 \pm 0.01\%$ (Table 3).

Table 3. The COD removal efficiency of the Fe(II)/Fe(III)-S(IV) air system in different raw waters.

Locations	COD (mg/l)	CODR (%) (Mean \pm SD)
Apátfalva (Well III.)	5.21 ± 0.02	88.5 ± 0.01
Apátfalva (Well IV.)	6.91 ± 0.01	88.1 ± 0.02
Biharkeresztes (Well III.)	7.88 ± 0.01	62.0 ± 0.01
Földeák (Well III.)	2.70 ± 0.01	85.5 ± 0.01
Kismarja (Well II.)	6.52 ± 0.02	81.8 ± 0.01
Makó (Well I-II-III.)	2.30 ± 0.01	85.4 ± 0.02
Nagyér (Well IV.)	3.20 ± 0.005	87.8 ± 0.01
Pocsaj (Well III.)	6.80 ± 0.01	81.0 ± 0.02
Pocsaj (Well IV.)	9.18 ± 0.01	82.9 ± 0.02

$$c_{\text{Fe}} = 1,7 \text{ mM}, Fe(II)\% = 20 \%, c_{\text{S(IV)}} = 0.9 \text{ mM } t_{\text{levegő}} = 42 \text{ perc}, \\ v_{\text{levegő}} = 200 \text{ ml/perc.}$$

3.4. We have confirmed that the ammonium ion content of the raw water is not altered by the oxidative pre-treatment with the Fe(II)/Fe(III)-S(IV)-air system. The breakpoint chlorination proceeds in the same way in the non-treated and oxidatively pre-treated raw water.

3.4.1. The breakpoint chlorination, i.e. the complete removal of ammonium ion, requires the same mass ratio of HOCl : NH₄⁺ in the non-treated and oxidatively pre-treated water which is 8.7 : 1 in all cases. This ratio corresponds to the 100 % dose of hypochlorite.

3.4.2. After the addition of 100% sodium hypochlorite dose to the samples, the chlorination reaction is somewhat slower in the oxidized sample than in the untreated sample. This difference is interpreted by considering that the oxidative pre-treatment decreases the COD by nearly 87 % in the raw water and, as a consequence, the matrix effect is significantly altered. However, the breakpoint chlorination is complete within 90 min. in all cases at room temperature.

3.5. We have demonstrated that the breakpoint chlorination produces substantially less trihalomethanes (THMs) and adsorbable halogenated organic compounds (AOXs) after the oxidative pre-treatment of the raw water with the Fe(II)/Fe(III)-S(IV)-air system.

3.5.1. The concentrations of AOX and THM decreased by 79.05 ± 2.10 % and 79.06 ± 15.36 %, respectively, in the raw water from Királyhegyes. After breakpoint chlorination, the THM concentration was close to the 50 µg/l regulation limit (Decree 201/2001 (X.25.) in the raw water, but the concentration of this contaminant dropped to 13 % of the limit value by oxidative pre-treatment.

3.5.2. The concentration of ammonium ion in raw water from different sources varies over a relatively wide range (0.22 - 1.58 mg/L), therefore the concentration of sodium hypochlorite required for breakpoint chlorination also varies significantly. In addition, there is an up to 2.5-fold difference in the concentration of organic precursors in the different raw waters. As a consequence, a clear correlation cannot be established between the composition of the raw waters and the concentration of THM and AOX formed. Nevertheless, the general trend is that higher organic matter content leads to the formation of chlorinated organic components in higher concentrations.

3.5.3. Oxidative pre-treatment of source waters from different geographic locations led to the decrease of the THM concentrations by 41.2 to 73.3 % (Figure 5) and the AOX concentrations by 61.3 to 84.1 % (Figure 6). In these pre-treatments the parameters optimized for the raw water from Királyhegyes were used.

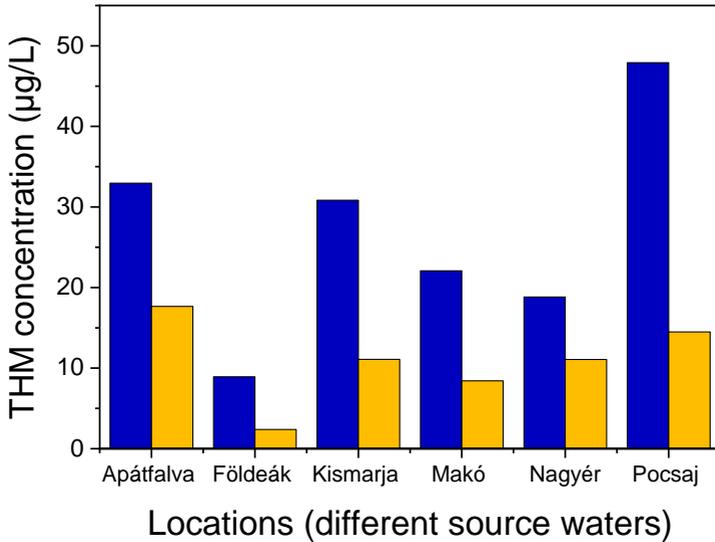


Figure 5. The THMs in raw and oxidatively pre-treated source waters from different locations after breakpoint chlorination.

Blue colour: untreated raw water, yellow colour: oxidatively pretreated raw water.

Sodium hypochlorite was used in 100 % dose which corresponds to the 8.7 HOCl to NH_4^+ mass ratio.

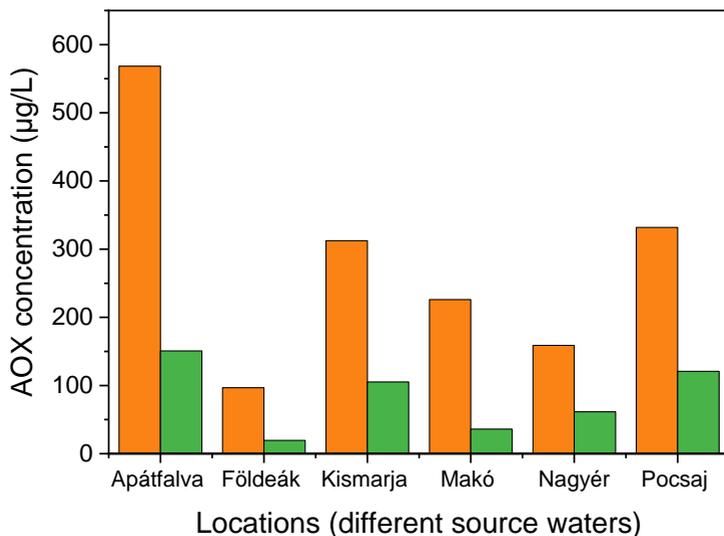


Figure 6. The AOX in raw and oxidatively pre-treated source waters from different locations after breakpoint chlorination.

Orange colour: untreated raw water, green colour: oxidatively pretreated raw water.

Sodium hypochlorite was used in 100 % dose which corresponds to the 8.7 HOCl to NH_4^+ mass ratio.

3.6. *We have shown that the oxidative pre-treatment also plays a significant role in the removal of microorganisms from the raw waters.*

3.6.1. Experiments on the formation biofilm layer confirmed that the oxidative treatment has a major impact on microorganism, as microscopic images did (in raw waters of Berekböszörmény and Pocsaj) after oxidation no longer showed any evidence of living organisms.

3.6.2. Microscopic images of the raw water taken from Well 2. in Biharkeresztes showed *Crenothrix polyspora* filamentous iron bacteria and roundworm (*Rotatoria*). These microorganisms were removed by the oxidative treatment.

3.6.3. The *Colony count of bacteria growing at 37°C* was 50/ml before oxidative treatment in the Pocsaj raw water taken in sterile samples. It is more than twice of the 20/ml limit allowed according to the government regulation. This high bacterial count indicates the formation of a biofilm layer, which was confirmed by microscopic biological studies. It was confirmed that the colony count is reduced to 2/ml after the oxidative treatment, which corresponds to a 96 % removal efficiency.

3.6.4. The *Colony count of bacteria growing at 22°C* in the untreated raw water was initially 42/ml, but was completely removed by oxidative treatment.

3.6.5. The *Colony count of bacteria growing at 37°C* in untreated raw water from Berekböszörmény is 195/ml, which is more than 9 times the limit of 20/ml set by the government regulation; while the *colony count of bacteria growing at 22°C* is 260/ml, which is more than 2 times the limit of 100/ml set by the government regulation. These high colony counts indicate biofilm formation or a localized problem, however, microscopic biological studies confirm the presence of biofilm.

3.6.6. Due to the oxidative treatment of the Berekböszörmény raw water with the Fe(II)/Fe(III)-S(IV)-air system, the *colony counts of bacteria growing at 37°C* were completely removed, while the *colony counts of bacteria growing at 22°C* were reduced to 2/ml. By reducing the colony count of bacteria in raw water, the pre-treated raw water becomes biologically more stable that helps to prevent possible bacterial contamination in the distribution networks, i.e. to minimise secondary effects.

V. POSSIBLE UTILIZATION OF THE RESULTS

Chemical oxygen demand (COD) in source waters presents a major challenge for drinking water treatment plants. The method presented in the dissertation offers a versatile alternative for decreasing COD compared to other techniques used before. In our work, we have studied the Fe(II)/Fe(III)-S(IV)-air oxidative system in detail. This is one of the most efficient, yet environmental friendly oxidant and disinfectant system known today.

The main advantage of this process is that only harmless products form from the applied reagents. Iron is transferred into iron(III) precipitate which can be removed in later steps of the water treatment technology, and the added sulfur(IV) is completely oxidized to sulfate ion in the process. Most importantly, the concentrations of the reagents and the final products are way below the regulatory limit after the treatment. In this study, the source water was used as received, i.e., no pretreatment is required to achieve high-efficiency COD removal. The use of Fe(II)/Fe(III)-S(IV)-air treatment in the early stage of drinking water production is also expected to reduce the risk of the formation of antagonistic products in further steps of the overall technology. Furthermore, it has been shown that this oxidative treatment is suitable to inactivate various chlorine-resistant polluting microorganisms in the raw water.

Our results also confirm that after the oxidative pre-treatment, which removes a significant part of the organic pollutants, the concentration of harmful by-products formed during the breakpoint chlorination process is significantly reduced in raw water. Therefore, the application of the Fe(II)/Fe(III)-S(IV)-air system has the potential to improve water quality and prevent secondary water quality problems in the water distribution network.

LIST OF PUBLICATIONS

List of publications related to the dissertation

Foreign language scientific articles in international journals (2)

1. **A. Truzsi, B. Kovács, I. Bodnár, I. Fábián**
Controlling the formation of halogenated byproducts in the chlorination of source waters by oxidative pre-treatment with the Fe(II)/Fe(III)-S(IV)-air system
Ecotoxicology and Environmental Safety, **2022**, 244, 114036.
DOI: 10.1016/j.ecoenv.2022.114036
[D1, IF.: 7.129, Cit.: 0/0]
2. **A. Truzsi, J. Elek, I. Fábián**
Sulfur(IV) assisted oxidative removal of organic pollutants from source water
Environmental Pollution, **2022**, 294, 118625.
DOI: 10.1016/j.envpol.2021.118625
[D1, IF.: 9.988, Cit.: 0/0]

List of other publication

Hungarian scientific articles in Hungarian journals (5)

1. **Truzsi A., Szmolka M., Bodnár I., Varga J.**
Oxidációs eljárások összehasonlítása neonikotinoid növényvédő szerek modelloldatokból történő eltávolítására
Int. J. Eng. Manag. Sci., **2019**, 4 (2), 91-98
DOI: 10.21791/IJEMS.2019.2.11.

2. **Truzsi A., Bodnár I., Fülöp Z.**
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List of publications related to the dissertation

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1. **Truzsi, A.**, Kovács, B., Bodnár, I., Fábíán, I.: Controlling the formation of halogenated byproducts in the chlorination of source waters by oxidative pre-treatment with the Fe(II)/Fe(III)-S(IV)-air system.
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