# Groundwater Treatment using the Fenton process: Changes in Natural Organic Matter Characteristics and Arsenic Removal

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**ABSTRACT:** This work investigates the use of Fenton's process (pH 5.5 and 6; 0.10-0.50 mM Fe(II); molar ratios Fe(II) to  $H_2O_2$  of 1:5-1:20) combined with flocculation for the treatment of groundwater which is rich in natural organic matter (NOM) (10.6±0.37 mg C/L) and arsenic (110±6.7 µg/L). Changes to the character of the residual NOM fractions were followed, as well as the removal efficiencies of NOM and arsenic. Under optimal reaction conditions at pH 5.5, 55% of the Dissolved Organic Carbon (DOC) was removed, whilst removals of specific disinfection by-product precursors of trihalomethanes (THM), haloacetic acids (HAA) and haloacetonitriles (HAN) were 80%, 75% and 98%, respectively. Total arsenic concentrations were reduced to below 5 µg/L under all investigated experimental conditions. After the Fenton treatment, the percentage of the hydrophobic NOM fraction (humic acid and fulvic acid fraction) decreased, and the percentage of the hydrophilic fraction (acidic and non-acidic fractions) increased. The hydrophilic fraction, which was the most abundant in the treated water, was also the most reactive fraction towards THM and HAA formation, whereas the residual fulvic acid fraction of HAN.

Key words: Natural organic matter, Arsenic, Water treatment, Fenton's process, Disinfection by-products

#### INTRODUCTION

Natural Organic Matter (NOM) is present in all surface, ground and soil waters. The NOM present in drinking water sources plays an important role during drinking water treatment, influencing the efficiency of many water treatment processes, including the performance of unit processes (i.e. oxidation, coagulation and adsorption) and the application of Disinfectants. The role of NOM as a precursor to Disinfection By-Products (DBPs) formation is particularly significant. More than 600 DBPs have been identified in drinking water to date, and many have been found to be hazardous to human health, in particular showing carcinogenic effects. The chemistry associated with oxidation/disinfection in water is complex due to differences which exist in NOM structure, particularly the distribution of the hydrophobic and hydrophilic NOM fractions, as well as the presence of bromide/iodide, water alkalinity etc. (Von Gunten, 2003; Krasner et al., 2006; Matilainen et al., 2011; Molnar et al., 2013). Two classes of DBPs, the trihalomethanes (THMs) and the haloacetic acids (HAAs), are considered to be the most commonly found chlorinated DBPs in drinking water (Krasner et al., 2006; Bond et al., 2009; Sarathy and Mohseni, 2010). The

Nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HANs), halonitromethanes (HNMs) and haloacetamides also occur in drinking water in lower concentrations than the THMs and HAAs, but are all far more cytotoxic and genotoxic (Bond *et al.*, 2012). Furthermore, NOM can play an important role in increasing the mobility of arsenic in aquifers, such that many groundwaters which are naturally contaminated with arsenic also contain high levels of NOM.

NOM is a complex and variable mixture of organic compounds of biological and terrestrial origin, so it is therefore expected to show different reactivities for DBPs formation, depending upon its origin and structure. Knowledge of the identity of DBP precursors can allow the selection of appropriate processes for their removal (Bond *et al.*, 2009). Generally, the hydrophobic NOM fraction is thought to be the most important precursor for THM and HAA formation (Kitis *et al.*, 2002; Liang and Singer, 2003; Tubić *et al.*, 2013). In addition, some researchers have reported that the hydrophobic fraction is not always the primary source of THM precursors, with the hydrophilic/polar fraction bearing the highest amount of THM precursors of all the NOM fractions

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(Chiang *et al.*, 2009; Tubić *et al.*, 2013). Similarly, dissolved organic nitrogen (DON), which contains a complex mixture of amino acids, amino sugars, amides, peptides and heterocyclic-N compounds of low molecular weight and low hydrophobicity, is the main precursor of N-DBP (Westerhoff and Mash, 2002; Chu *et al.*, 2012).

Meanwhile, the contamination of groundwater with arsenic has attracted worldwide attention. Arsenic(III) is classified as a group I carcinogen by the International Agency for Research on Cancer (IARC, 2012). The World Health Organization (WHO, 2011) has established 10 µg/ L as the maximum allowable arsenic concentration for drinking water. Arsenic removal from water by conventional technologies usually requires a preoxidation of As(III) to As(V) in order to achieve a satisfactory total arsenic removal (USEPA, 2001). NOM has been shown to be an essential component controlling arsenic mobilization and behaviour during water treatment (Liu et al., 2008; Mohora et al., 2012), and as such, groundwaters containing elevated arsenic levels may also have high NOM contents. In their review, Matilainen and Sillanpää (2010) outline the use of different advanced oxidation processes (AOPs) to degrade NOM and thus minimize DBP production. Among these hydroxyl radical generating processes, Fenton and photo-Fenton processes have been extensively investigated over the last decade for NOM and humic substances removal, as well as arsenic removal, and are generally more effective at low pH. In the Fenton process, iron salts initiate and catalyze the decomposition of H<sub>2</sub>O<sub>2</sub>, resulting in the generation of hydroxyl radicals (Wu et al., 2010). The Fenton process proceeds in aqueous solutions by complex reaction mechanisms, with the removal of organic matter involving oxidation, coagulation and precipitation (Murray and Parsons, 2004; Goslan et al., 2006; Moncayo-Lasso et al., 2009, 2012; Wu et al., 2010). These studies focused mostly on the use of Fenton's process to remove total organic matter on the basis of DOC and UV<sub>254</sub> content, with little information on the removal of hazardous disinfection by--products precursors. Our previous research has shown that at pH 5, Fenton's process was very effective at removing NOM and commercial humic acids, as well as THMs and HAAs precursors. However, the NOM oxidation lead to slight increases in N-DBPs formation (Molnar et al., 2011). In addition, Murray and Parsons (2004) and Kalajdžić et al. (2013) state that Fenton's process may be successfully used for NOM removal and THMFP reduction in groundwater. However, although it has been established that Fenton's process is effective for arsenic oxidation and removal from groundwater (Banerjee et al., 1999; Krishna et al., 2001), the effects of the presence of NOM on arsenic behaviour during the Fenton process

have not yet been shown. Furthermore, the effect of Fenton's process on the structure of NOM and the reactivity of the different NOM fractions towards DPB formation during the Fenton process is yet to be investigated. This research therefore investigates the effects of Fenton's process in changing the character of NOM and removing arsenic from groundwater, whilst also investigating the contribution of the individual NOM fractions isolated after the Fenton process towards the formation of hazardous chlorinated and brominated disinfection by-products. Having previously proven the high efficiency of Fenton's process at low pH values, this paper focuses on the application of Fenton's process at higher pH values in combination with flocculation, as significant correction of pH during drinking water treatment can be expensive.

### MATERIALS & METHODS

Laboratory studies were made using groundwater from Vojvodina, Serbia, which contains high levels of arsenic (110±6.7 µg/L) and natural organic matter (10.6±0.37 mg-/L DOC). The NOM is mostly of hydrophobic character (68% fulvic acid-FAF and 14% humic acid fraction-HAF), with the hydrophilic fraction making up only 18% of DOC (Tubić et al., 2013). The formation potentials of the trihalomethanes and haloacetic acids were  $422\pm53 \mu g$ -/l and  $363\pm31 \mu g$ -/l, respectively, and significantly lower for haloacetonitrile formation potential ( $18.5\pm8.1 \mu g$ -/l). The total arsenic content was 110±6.7 µg/L. The dominant species of As in the raw groundwater is As(V) (42%), followed by As(III) (35.2%) and organically bonded As (22.8%). More detailed raw groundwater characteristics are given in Tubić et al. (2010).

Ferrous sulphate heptahydrate (POCH SA, CAS No. 7782-63-0) and 30% w/w reagent grade H<sub>2</sub>O<sub>2</sub> (POCH S.A., CAS No.7722-84-1) were used in the Fenton process experiments. Supelite<sup>™</sup> DAX-8 resin from Supelco and Amberlite XAD-4 resin from Fluka were used in the NOM fractionation procedure. Resins were purified by Soxhlet extraction according to the standard method (AWWA-APHA-WEF, 2012) and packed separately into glass columns for further NOM isolation. Standards for trihalomethanes (chloroform, CF: bromodichloromethane, BDCM: dibromochloromethane, DBCM and bromoform, BF), haloacetic acids (monochloroacetic acid, MCAA; monobromoacetic acid, MBAA; dichloroacetic acid, DCAA; trichloroacetic acid, TCAA; bromochloroacetic acid, BCAA and dibromoacetic acid, DBAA) and haloacetonitriles (trichloroacetonitrile, TCAN; dichloroacetonitrile, DCAN, bromochloroacetonitrile, BCAN and dibromoacetonitrile, DBAN) analysis with concentrations of 2000 µg/mL were purchased from Supelco. The solvents methanol, acetone, methyl tertbutyl ether, hexane, acetonitrile and diethyl ether were obtained from JT Baker (for organic residue analysis).

The efficiency of the Fenton process for removing NOM and arsenic was investigated at two pH values (pH 5.5 and 6.0). The jar test experiments were carried out on a FC6S Velp Scientifica apparatus in 1L beakers at room temperature (23 °C). The pH was measured on a WTW InoLab instrument, and was adjusted prior to the jar test experiments. To 0.6 L of raw water, aliquots of iron(II) sulphate heptahydrate and hydrogen peroxide were added simultaneously to obtain the corresponding concentrations of Fe(II) (0.10-0.50 mM) and molar ratios to  $H_2O_2$  (1:5-1:20). The effect of the reaction time (1-30) min) was also investigated. After the simultaneous addition of Fe(II) salt and H<sub>2</sub>O<sub>2</sub> water samples were subjected to rapid stirring (200 rpm) for 1 minute followed by mixing at 30 rpm for 1-30 min, depending on the reaction time investigated. After stirring, sample pH was adjusted to pH7, flocculant Magnaflok LT26 (0.2 mg/L) was added in order to improve floc consolidation and stirring was continued for another 25 min. After the jar tests, the samples were left to stand for 30 min, to allow settling of the formed floccules. Upon clarification and separation of the supernatant from the iron flocs, the water samples were filtered through a glass fibre filter  $(0.6 \,\mu\text{m})$  prior to analysis, to remove residual particulate matter. The efficiency of the Fenton process was followed on the basis of the contents of arsenic, DOC and  $UV_{254}$ . In addition, changes in the NOM structure were also investigated, with particular emphasis on the disinfection by-products formation of the trihalomethanes, haloacetic acids and haloacetonitriles.

Changes in the NOM structure after the Fenton process were determined by fractionation in glass columns, filed with XAD resins according to Goslan et al. (2002). After filtration through a 0.45 µm membrane filter, water samples were analyzed for DOC content on an Elementar LiquiTOCII. UV<sub>254</sub> absorbance measurements were performed in accordance with standard methods (AWWA-APHA-WEF, 2012) on a CINTRA 1010, GBC Scientific Equipment spectrophotometer at a wavelength of 254 nm with a 1 cm quartz cell, and the SUVA (expressed in Lmg<sup>-1</sup>m<sup>-1</sup>) was calculated. Arsenic contents were analysed by ICP/MS (PE SCIEX ELAN 5000), and the method detection limit and method quantitation limit were 0.1 and 0.5  $\mu$ g/L, respectively. As recoveries at 100 µg/Lwere 90-110%. pH measurements were carried out on a WTW InoLab portable instrument. Disinfection by-products formation potential (DBPFP) was determined according to the standard method for measuring THMFP (AWWA-APHA–WEF, 2012). At the end of the 7-day reaction period, the samples were dechlorinated, and THMs, HAAs and HANs were analyzed. THMs were directly analyzed with a purge and trap system (Tekmar 3100) coupled to a gas chromatograph (Agilent Technologies 7890A) equipped with mass selective detector (Agilent Technologies 5975C), based on USEPA methods 5030B and 8260B. HAAs and HANs were determined by liquidliquid extraction with methyl tert-butyl ether followed by analysis by GC/µECD instrument (Agilent 6890N), according to USEPA methods 552.2 and 551.1. The practical quantitation limits (PQL) for the investigated DBPs are given in Molnar et al. (2012). The recoveries for spiked water samples in the concentration range 1-100 µg/L were 78-118% for THM, 83-128% for HAA and 89-108% for HAN analysis. The specific formation potentials (FP) were calculated as the ratios between the THMFP, HAAFP or the HANFP and the DOC for each NOM fraction.

# **RESULTS & DISCUSSION**

The results from investigating the effects of the pH (pH 5.5 and 6.0) and reaction time (1-30 min) on Fenton process efficacy for NOM removal are presented in Fig. 1. As was expected, NOM was more efficiently removed by Fenton's process at pH 5.5 (up to 48% DOC removal) than pH 6.0 (up to 30% DOC removal), with the greatest efficacy achieved using a higher dose of 0.25 mM Fe(II). NOM removal by Fenton's process at pH 6.0 was nearly the same as coagulation alone using iron(III) salts (Tubić *et al.*, 2010), indicating that Fenton's process did not have a significant impact on the degree of NOM removal at this pH, with NOM removal likely occurring mainly due to coagulation. After 5 min of Fenton process, there were no further reductions in the total organic matter content at both investigated pH levels.

The results presented here were compared with results for a similar water type obtained in a previous study which applied Fenton's process at pH 5.0 with an optimal reaction time of 15 min. (Molnar et al., 2011). It is possible a different NOM mechanism is involved depending on the pH of the process. It can be supposed that increasing the pH leads to a faster consumption of Fe(II), due to its precipitation in the form of ferric hydroxide. This would result in the loss of Fe(II) as a catalyst and further inhibit the catalytic reaction of Fe(II) with the oxidant, resulting in less NOM oxidation. The efficiency of the process at pH 5.5 was lower than at pH 5.0, where a reduction of 80% DOC was achieved after a 15 min reaction time (Molnar et al., 2011). According to the results obtained, the optimal reaction time for the Fenton process at pH 5.5 and 6.0 is 5 min. At pH 6.0, there was a high residual content of NOM after the Fenton process (7.25 mg/L DOC), and so further experiments (investigation of the effect of initial reagent dose) were conducted only at pH 5.5, due to the more efficient removal of NOM under these conditions. After determining the optimal reaction time at pH 5.5, the effect



Fig. 1. The effects of pH and reaction time on the efficacy of the Fenton process at removing NOM from water

of the initial Fe(II) dose (0.10-0.50 mM) and the molar ratio of Fe(II):H<sub>2</sub>O<sub>2</sub> (1:5-1:20) on Fenton process efficiency with regards to arsenic and NOM removal was investigated (Fig. 2). Previous studies have shown that at pH 5.0, the Fenton process more efficiently removes total NOM (up to 80% DOC) at a higher dose of Fe(II) and a lower molar ratio of Fe(II):H<sub>2</sub>O<sub>2</sub> (Molnar et al., 2011). A similar trend was observed after applying the Fenton process at pH 5.5, but with lower process efficiency (up to 55% DOC removed). At all investigated Fe(II):H<sub>2</sub>O<sub>2</sub> molar ratios, the application of the lower 0.1 mM Fe(II) dose did not result in a significant reduction in NOM content. Increasing the Fe(II) dose resulted in better NOM removals, whereby the most effective dose for total organic matter removal was 0.25 mM Fe(II) at a molar ratio of 1:5 with H<sub>2</sub>O<sub>2</sub> (55% removal of DOC). Increasing the dose of Fe(II) and H<sub>2</sub>O<sub>2</sub> further did not significantly improve the removal of NOM. The higher efficiency of the Fenton process at lower pH values was also observed by the authors Murray and Parsons (2004) and Goslan et al. (2006). Under optimal process conditions (at pH 4-5), they successfully removed organic components from the water, with greater than 90% reduction in DOC. Comparing the results of these studies with coagulation for similar water types, it should be noted that Fenton's process was more effective in removing NOM than conventional coagulation with FeCl, with a similar dose of iron salt (Tubiæ et al., 2010).

The optimal 0.25 mM dose of Fe(II) (Fig. 3) was used to investigate the removal of specific precursors of trihalomethanes, haloacetonitriles and haloacetic acids. The efficiency of the Fenton process was shown to increase with an increasing molar ratio of Fe(II):H<sub>2</sub>O<sub>2</sub>,



Fig. 2. The effects of Fe(II) dose and Fe(II):H<sub>2</sub>O<sub>2</sub> molar ratio on the changes in DOC

whereby reductions increased from 39 to 80% for THMFP, from 31 to 75% for HAAFP, and from 81 to 98% for HANFP. It can be assumed that these results are a consequence of the increased production of hydroxyl radicals generated at higher concentrations of hydrogen peroxide, where the specific DBP precursors were very effectively removed by oxidation, coagulation and precipitation. The results also indicate that the Fenton process is considerably more effective in reducing THMs precursors than conventional coagulation, where THMFP reductions of around 45% have been reported (Tubić *et al.*, 2010).

Table 1 shows the results from investigating the effect of Fe(II) dose and Fe(II):H<sub>2</sub>O<sub>2</sub> molar ratio on arsenic removal by the Fenton process. At pH 5.5, the process was highly effective at removing arsenic, with at least 96% of the arsenic present removed under all investigated conditions. The residual arsenic concentrations after the Fenton process were therefore all below the 10 µg As/L limit (WHO, 2011), and also below the quantification limit of As speciation method. Authors Banerjee et al. (1999) also showed a high degree of As removal by Fenton process, even at lower molar ratios of Fe(II) and  $H_2O_2$ . They reported that the Fenton process showed the highest efficiency at pH 2.5-3 with a Fe(II):H<sub>2</sub>O<sub>2</sub> mass ratio of 1:2. More than 99% of the arsenic was removed during the first five minutes of the reaction. However, during the optimization process, it is always necessary to bear in mind the nature of the water matrix, which in the case of the water investigated in this paper, includes a high NOM content and high alkality of 695±7.5 mg CaCO,/ L (Tubic et al., 2010), making it necessary to apply a higher dose of the reagents for effective NOM removal.



Fig. 3. The effect of Fenton's process at pH 5.5 on the formation potentials of trihalomethanes, haloacetic acids and haloacetonitriles

Table 1. Effects of Fe(II) dose and Fe(II):H<sub>2</sub>O<sub>2</sub> molar ratios on the removal of arsenic from water by the Fenton process at pH 5.5

Fe(II) (mM)	Fe(II): H <sub>2</sub> O <sub>2</sub> molar ratio	As (µg/L)
Raw water		110±6.7
0.10	1:5	1.23±0.21
	1:10	$4.38 \pm 0.78$
	1:20	$2.44 \pm 0.47$
0.25	1:5	< 0.50
	1:10	< 0.50
	1:20	<0.50
0.50	1:5	< 0.50
	1:10	< 0.50
	1:20	< 0.50

Authors Tubic *et al.* (2010) and Baskan and Pala (2009) have shown that the removal of arsenic is effective even with ferric chloride coagulation, but several substances that are commonly found in natural water, including bicarbonate and NOM, interfere with arsenic removal.

The changes caused by the Fenton process to the character of NOM present in the water were investigated at an applied Fe(II) dose of 0.25 mM and an Fe(II): $H_2O_2$  molar ratio of 1:20 at pH 5.5. These were the optimum conditions for the specific DBPs precursors found during the previous phase of the experiment. The NOM characterisation results show that applying the Fenton process at pH 5.5 results in significant changes in the NOM structure (Fig. 4). Compared to the NOM distribution in the raw water (Tubić *et al.*, 2013) the humic acid fraction was completely removed, the fulvic acid fraction content



Fig. 4. Effect of the Fenton process (0.25 mM Fe(II); molar ratio Fe(II):H<sub>2</sub>O<sub>2</sub>1:5, pH 5.5) on the character of the residual NOM

decreased and the contribution of residual hydrophilic NOM increased by up to 79% (75% of the hydrophilic non-acidic fraction, HPI-NA and 4% of hydrophilic acid fraction, HPIA) in the treated water. The residual hydrophilic acid fraction, although present in the lowest amount (only 4%), was the most reactive NOM fraction in terms of THMs formation, representing 56.6% (90.4  $\mu$ g/mg DOC) of the specific THMFP. The fulvic acid fraction represents slightly less of the NOM reactivity with 43% (68.8 µg/mg DOC), while the hydrophilic non-acid fraction, although dominant in the treated water, showed the lowest reactivity towards THM formation, contributing only 0.4% (0.574  $\mu$ g/ mg DOC) (Fig. 5a). In all the NOM fractions after the Fenton process, chloroform precursors dominated (87-98%), followed by BDCM (2-10%) and DBCM (up to 0.9%) precursors, whereas bromoform precursors were not detected in the treated water. The results also indicate that the hydrophilic fraction is slightly more reactive for brominated THM formation than the hydrophobic fulvic acid fraction (Fig. 5b).

The distribution of HAA precursors in the NOM fractions after the Fenton process is similar to that THM precursors. The residual hydrophilic acid fractions proved to be the most reactive towards the formation of haloacetic acids, contributing 60.3% (80.1  $\mu$ g/mg DOC) of the specific HAAFP. The fulvic acid fraction contributes less to the total HAA formed with 39.5% (52.5 µg/mg DOC), while the hydrophilic nonacid fraction, although the most dominant in the water after the Fenton process, was the least reactive towards the formation of HAA (less than 0.5%) (Fig. 6a). After chlorination of the isolated NOM fractions, the dominant HAA formed were MBAA (in the case of FAF and HPIA) and TCAA which was the most commonly formed HAA in HPI-NA. BCAA and DBAA precursors in the NOM fractions had much lower





contents (up 0.2%). The results also indicate that in addition to the hydrophilic NOM fractions, the fulvic acid fraction also contributes significantly to the formation of MBAA, one of the brominated HAA (Fig. 6b). Comparing the results of treated water with the result of the characterization of the raw water (where the most reactive fraction for the formation of THM and HAA was the hydrophobic humic acid fraction) (Tubić *et al.*, 2013; Molnar *et al.*, 2012), it can be seen that the Fenton process had a significant impact not only on the content of THM and HAA precursors, but also on their distribution in the treated water. The specific THMFP and HAAFP suggest that the Fenton process also had a significant impact on the reactivities of the residual NOM fractions.

In contrast to the behaviour of the THM and HAA precursors, haloacetonitrile precursors are more present in the fulvic acid fraction (78%) than the hydrophilic fraction (22% for HPIA). In the hydrophilic non-acid fraction, HAN precursors were not detected (Fig. 7a). The most commonly formed HAN compound



Fig. 6. a) The pie charts depict each fraction's contribution to the total HAA precursors content. b) Distribution of HAA precursors as specific HAAFP in the NOM fractions of the treated water

after chlorination of the treated water was DBAN (91-100%), with DCAN only forming in the FAF fraction (a contribution of 9%), whereas BCAN and TCAN precursors were not detected in the treated water. The HAN results are similar to those of the THMs and HAAs, with the hydrophilic fraction again being slightly more reactive for the formation of the brominated DBAN, in comparison to the hydrophobic fraction (Fig. 7b). However, precursors of HAN are present in much smaller amounts than the THM and HAA precursors, contributing only 0.129 and 0.465  $\mu$ g/ mg DOC in the HPIA and FAF, respectively.

## CONCLUSIONS

This work investigated the changes caused to the character of the residual NOM by the Fenton process, as well as its efficiency for the removal of natural organic matter and arsenic from groundwater. Hydrophobic NOM was more efficiently removed by Fenton's process at pH 5.5 than at pH 6.0, probably due to the greater degree of NOM oxidation by OH



# Fig. 7. a) The pie charts depict each fraction's contribution to the total HAN precursors content. b) Distribution of HAN precursors as specific HANFP in the NOM fractions of the treated water

radicals and subsequent precipitation at lower pH. Under all investigated Fenton's process conditions, arsenic contents were reduced to less than  $5 \mu g/L$ .

NOM fractionation showed that applying the Fenton process at pH 5.5 results in significant changes in both NOM structure and reactivity for forming disinfection by-products. The humic acid fraction was completely removed, the fulvic acid fraction content decreased and the percentage of residual hydrophilic NOM increased in the treated water. The residual hydrophilic acid fraction was the most reactive NOM fraction in terms of THM and HAA formation, whereas the fulvic acid fraction was the most reactive in terms of HAN formation.

Although previous studies have shown that the Fenton process is most efficient at low pH, the results of this study indicate that a significant reduction of NOM can also be achieved at pH 5.5. However, the residual of total NOM (about 5-6 mg/L DOC) and their reactivity towards DBP formation suggests that it may be necessary to combine Fenton's process with other technologies in order to achieve quality drinking water.

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#### REFERENCES

AWWA–APHA–WEF (2012). Standard Methods for the Examination of Water and Wastewater, 21th ed., American Public Health Association/American WaterWorks Association/Water Environment Federation, Washington, DC.

Banerjee, K., Helwick, R.P., and Gupta, S. (1999). A treatment process for removal of mixed inorganic and organic arsenic species from groundwater. Environ. Prog. **18** (4), 280-284.

Baskan, M.B., and Pala, A. (2009). Determination of arsenic removal efficiency by ferric ions using response surface methodology. J. Hazard. Mater. **166** (**2-3**), 796-801.

Bond, T., Goslan, E.H., Jefferson, B., Roddick, F., Fan, L., and Parsons, S.A. (2009). Chemical and biological oxidation of NOM surrogates and effect on HAA formation. Water Res. **43** (**10**), 2615-2622.

Bond, T., Templeton, M.R., and Graham, N. (2012). Precursors of nitrogenous disinfection by-products in drinking water-A critical review and analysis. J. Hazard. Mater. **235–236 (15)**, 1-16.

Chiang, P.C., Chang, E.E., Chang, P.C., and Huang, C.P. (2009) Effects of pre-ozonation on the removal of THM precursors by coagulation. Sci. Total. Environ. **407** (**21**), 5735–5742.

Chu, W., Gao, N., Yin, D., Deng, Y., and Templeton, M.R. (2012). Ozone-biological activated carbon integrated treatment for removal of precursors of halogenated nitrogenous disinfection by-products. Chemosphere 86 (11), 1087–1091.

Goslan, E.H., Fearing, D.A., Banks, J., Wilson, D., Hills, P., Campbell, A.T., and Parsons, S.A. (2002). Seasonal variations in the disinfection byproduct precursor profile of reservoir water. J. Water Res. Technol. – AQUA 51, 475–482.

Goslan, E.H., Gurses, F., Banks, J., and Parsons, S.A. (2006). An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes. Chemosphere **65** (7), 1113-1119.

International Agency for Research on Cancer (2012). Chromium, Nickel and Welding, IARC Monographs on the Education of Carcinogenic Risks to Humans, 49. World Health Organization Lyon, France. Kalajdžić, B., Habuda-Stanić, M., Romić, Ž., and Kuleš, M. (2013). Removal of natural organic matter from groundwater using Fenton's process. Global NEST J. **15** (1), 13-20.

Kitis, M., Karanfil, T., Wigton, A., and Kilduff, J.E. (2002). Isolation of dissolved organic matter (DOM) from surface waters using reverse osmosis and its impact on the reactivity of DOM to formation and speciation of disinfection byproducts. Water Res. **35** (9), 2225–2234.

Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Sclimenti, M.J., Onstad, G.D., and Thruston, A.D. (2006). Occurrence of a new generation of disinfection byproducts. Environ. Sci. Technol. **40** (23), 7175–7185.

Krishna, M.V.B., Chandrasekaran, K., Karunasagar, D., and Arunachalam, J. (2001). A combined treatment approach using Fenton's reagent and zero valent iron for the removal of arsenic from drinking water. J. Hazard. Mater. **84** (2–3), 229-240.

Liang. L., and Singer, P.C. (2003). Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. Environ. Sci. Technol. **37** (**13**), 2920–2928.

Liu, G., Zhang, X., Talley, J.W., Neal, C.R., and Wang, H. (2008). Effect of NOM on arsenic adsorption by  $TiO_2$  in simulated As(III)-contaminated raw waters. Water Res. **42** (8-9), 2309-2319.

Matilainen, A., and Sillanpää, M. (2010). Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere **80** (4), 351-365.

Matilainen, A., Gjessing, E.T., Lahtinen, T., Hed, L., Bhatnagar, A., and Sillanpaa, M. (2011). An overview of the methods used in the characterization of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere **83 (11)**, 1431–1442.

Mohora, E., Rončević, S., Dalmacija, B., Agbaba, J., Watson, M., Karlović, E., and Dalmacija, M. (2012). Removal of natural organic matter and arsenic from water by electrocoagulation/flotation continuous flow reactor. J. Hazard. Mater. 235-236, 257-264.

Molnar, J., Agbaba, J., Dalmacija, B., Rončević, S., Maletić, S., and Kragulj, M. (2011). A Study on the Removal of Natural Organic Matter and Disinfection By-products Formation Potential from Groundwater Using Fenton's Process. J. Adv. Oxid. Technol. **14** (1), 54-62.

Molnar, J., Agbaba, J., Dalmacija, B., Klašnja, M.T., Dalmacija, M., and Kragulj, M. (2012). A comparative study of the effects of ozonation and  $\text{TiO}_2$ -catalyzed ozonation on the selected chlorine disinfection by-product precursor content and structure. Sci. Total. Environ. **425** (**15**), 169-175.

Molnar, J.; Agbaba, J.; Dalmacija, B.; Tubić, A.; Krčmar, D.; Maletić, S.; Tomaševic, D. (2013) The effects of matrices and ozone dose on changes in the characteristics of natural organic matter. Chem. Eng. J., 222, 435–443.

Moncayo-Lasso, A., Sanabria, J., Pulgarin, C., and Benítez, N. (2009). Simultaneous E. coli inactivation and NOM degradation in river water via photo-Fenton process at natural pH in solar CPC reactor. A new way for enhancing solar disinfection of natural water. Chemosphere **77** (2), 296-300.

Moncayo-Lasso, A., Rincon, A-G., Pulgarin, C., and Benitez, N. (2012). Significant decrease of THMs generated during chlorination of river water by previous photo-Fenton treatment at near neutral pH. J. Photoch. Photobio. A. **229** (1), 46-52.

Murray, C.A., and Parsons, S.A. (2004). Removal of NOM from drinking water: Fenton's and photo-Fenton's processes. Chemosphere **54** (7), 1017-1023.

Sarathy, S., and Mohseni, M. (2010). Effects of  $UV/H_2O_2$  advanced oxidation on chemical characteristics and chlorine reactivity of surface water natural organic matter. Water Res. **44 (14)**, 4087-4096.

Tubić, A., Agbaba, J., Dalmacija, B., Ivančev-Tumbas, I., and Dalmacija, M. (2010). Removal of arsenic and natural organic matter from groundwater using ferric and alum salts: A case study of central Banat region (Serbia). J. Environ. Sci. Heal A 45 (3), 363–369.

Tubić, A., Agbaba, J., Dalmacija, B., Molnar, J., Maletić, S., Watson, M., and Ugarčina Perović, S. (2013). Insight into changes during coagulation in NOM reactivity for trihalomethanes and haloacetic acids formation. J. Environ. Manage. **118**, 153-160.

USEPA (2001). National primary drinking water regulations: arsenic and clarifications to compliance and new source contaminants monitoring. Fed. Regist. **66** (14), 6975–7066.

Von Gunten, U. (2003). Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Res. **37** (7), 1469–1487.

Westerhoff, P.K., and Mash, H. (2002) Dissolved organic nitrogen in drinking water supplies: a review. J. Water Supply Res. Technol. **51**, 415–448.

WHO (2011). Guidelines for drinking-water quality. World Health Organization, Geneva.

Wu, Y., Zhou, S., Qin, F., Zheng, K., and Ye, X. (2010). Modeling the oxidation kinetics of Fenton's process on the degradation of humic acid. J. Hazard. Mater. **179** (1-3), 533-539.