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Effects of O_3, O_3/H_2O_2 and Coagulation on Natural Organic Matter and Arsenic Removal from Typical Northern Serbia Source Water

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The objectives of this study were to investigate the effects of ozone and the O_3/H_2O_2 process on $FeCl_3$ coagulation efficiency for the removal of the high content of natural organic matter (NOM) and arsenic (As) from groundwater (DOC = 9.27 ± 0.92 mg/L; 51.7 ± 16.4 μg As/L). Arsenic and NOM removal mechanisms during coagulation/flocculation are well investigated. However, data concerning arsenic removal in the presence of NOM, which is the subject of this article, are still insufficient. Laboratory and pilot plant test results have shown that the competition of NOM and As for adsorption sites on the coagulant surface have great influence on coagulation/flocculation efficiency for their removal. With both oxidation pre-treatments, arsenic content after the coagulation process was less than 2.0 μg/L in treated water. Application of ozone has a lower influence on coagulation efficacy in terms of DOC reduction, compared to the O_3/H_2O_2 process with the same ozone dose.

Keywords arsenic; groundwater; natural organic matter; O_3/H_2O_2 process; ozone

INTRODUCTION

Vojvodina is an autonomous province of the Republic of Serbia, and for the social and economic life of this region, groundwater is of vital importance, as the entire population and significant parts of industry and the agro-industry are completely oriented around this groundwater. One of the basic problems for a large number of communities in Vojvodina and the most common cause of the unacceptable drinking water quality, is the naturally occurring high contents of arsenic (As) and natural organic matter (NOM).

Arsenic is recognized as a great threat to human health and is classified as a Group I carcinogenic substance to humans, based on epidemiological evidence (1). The effects of arsenic exposure via drinking water include various types of skin lesions, neurological effects, peripheral vascular disease, cardiovascular disease, respiratory disease, as well as skin and other cancers (2). Therefore, organizations such as the World Health Organization (3), the Environmental Protection Agency (4), and Serbian legislation (5) include this parameter in their regulations and establish a maximum allowed level (MAL) for arsenic in drinking water at 10 μg/L. NOM affects water quality by increasing disinfectant and coagulant demand, providing precursor material for disinfection by-products (DBPs), and enhancing re-growth in distribution systems (6). In most cases in Vojvodina, water is chlorinated directly from the wells and released into the distribution system, so DBP formation poses one of the biggest issues of water quality. Some authors suggest that the formation of DBPs should be prevented, because once formed, they are hard to remove in treatments commonly used in drinking water production (7).

A variety of treatment processes have been developed for removing arsenic from water. The USEPA has identified seven best available technologies (BATs), based on a demonstration of efficacy under field conditions taking cost into consideration (Table 1). These methods are mainly effective for the removal of arsenate (4).

Nowadays, research has been directed towards identifying new technologies for arsenic removal, as well as on improving existing conventional technologies, by modifying or using novel adsorption materials or introducing new chemical oxidation processes. One of the most commonly used treatment methods for arsenic removal involves coagulation/flocculation (8), because of its low cost and high efficacy (9).

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TABLE 1
Best available technologies and their arsenic removal efficacies (4)

Treatment technology	Maximum removal (%)
Coagulation/Filtration	95
Activated alumina	95
Ion exchange	95
Lime softening ($pH > 10.5$)	90
Reverse osmosis	>95
Electrodialysis	85
Oxidation filtration	80

Some of the conclusions drawn from investigations of arsenic removal by the coagulation/flocculation process are that

(i) the main mechanism of this process involves adsorption, co-precipitation, and precipitation (10);
(ii) iron coagulants are more efficient than aluminium ones (11,12),
(iii) among the iron coagulants, ferrous-chloride is the most efficient (8)
(iv) arsenate (As^{5+}) is more efficiently removed than arsenite (As^{3+}) (10);
(v) the optimal pH value for effective As removal by $FeCl_3$ is around 7.0 (8);
(vi) pre-oxidation is necessary for better removal (13) and
(vii) several substances that are commonly found in natural water, including bicarbonate (14), and NOM (15) interfere with arsenic removal.

Chemical coagulation and subsequent solid-liquid separation processes have also been demonstrated to significantly remove NOM during drinking water treatment (7). According to the same authors, enhanced and optimized coagulation can be an economical alternative for improved NOM removal from raw water in comparison to GAC (as one of the BAT technologies for NOM removal) and membrane filtration processes. The main NOM removal mechanism by coagulation involves charge neutralization of colloidal NOM, precipitation as humates and fulvates, and co-precipitation by adsorption on metal hydroxides. Ferric chloride can be effectively used as a coagulation reagent for NOM removal. The effectiveness of coagulation/flocculation to remove NOM is affected by NOM nature, the dosage of the coagulant, and the pH value (7). Many authors have been interested in arsenic removal mechanisms during coagulation/flocculation (8,9,10). Additionally, the efficiency, mechanism, and operational conditions for NOM removal by coagulation/flocculation are well investigated (7,17). However, according to Pallier et al. (10), data concerning arsenic removal in the presence of NOM are still insufficient.

When arsenic is co-precipitated with iron hydroxide in a water plant, a large quantity of sludge is generated which contains a high amount of arsenic (18). Proper treatment and disposal of the sludge and waste materials is an important environmental and economic issue. Water treatment residuals are typically disposed of in landfills. However, in natural environments, competition of treatment residuals with other dissolved species for sorption sites can cause arsenic leaching. In order to prevent arsenic desorption, waste treatment residuals need to be stabilized. Solidification/stabilization (S/S) with cement, lime, and flying ash are commonly used for treatment of solids and contaminated sludge (19).

However, in some cases conventional treatment (coagulation with metal salts, sedimentation, and filtration) is unsatisfactory and other processes have to be applied (20,21). One way to improve conventional treatment in NOM and arsenic removal is the introduction of an oxidation step before coagulation (13,21). For this purpose, the mostly commonly used oxidation reagent is ozone. To improve the oxidation efficiency of ozone and subsequently coagulation process efficiency, a combination of ozone and hydrogen-peroxide (O_3/H_2O_2, PEROXONE®, process), can be also used (23). O_3/H_2O_2 is a process which belongs to the group of advanced oxidation processes (AOPs). AOPs allow the in-situ generation of highly reactive chemical oxidants such as hydroxyl radicals ($OH^{\cdot}$), and can destroy a wide range of organic contaminants in water, and thus in recent years they have been applied as a technological option for speeding up the oxidation process (24). However, data concerning application of O_3/H_2O_2 as a pre-treatment to improve NOM and arsenic removal in the coagulation/flocculation process is still insufficient.

This study aimed at investigating the possibilities of applying $FeCl_3$ in the coagulation process for arsenic and NOM removal from groundwater, and compare the effects of ozone and O_3/H_2O_2 processes on the efficiency of the coagulation/flocculation process, while removing large amounts of NOM present in the groundwater.

The originality of this work is based on investigation of arsenic removal from water with high NOM content. Literature data shows that the presence of these two constituents in water can lead to competition for adsorption sites on the coagulant surface, which greatly influences coagulation efficiency in removing As and NOM. This work also investigates the influence of the O_3/H_2O_2 process, as an oxidation reagent which is not often used in treatments applied to remove arsenic and NOM, and compares it with the effect of one commonly used oxidation pre-treatment (ozone) on coagulation/flocculation efficiency. The systematic investigation was conducted through laboratory experiments and pilot plant tests.

MATERIALS AND METHODS

Raw Water Characteristics

This study investigated groundwater from central Banat, Vojvodina region, Republic of Serbia. Water was drawn from a depth of 40–80 m and 100–150 m. It is groundwater from an artesian layer formed in pliocene-pleistocene sediments. The water is of the sodium-hydrocarbonated type, with high amounts of sodium, and low levels of magnesium and calcium. The hydrocarbonate ion is dominant amongst the anions, equivalent to 85–90%. The drinking water investigated has a high amount of NOM (DOC = 9.27 ± 0.92 mg/L). This organic content is geological in origin as the Vojvodina region (especially the Banat region) lies in the south-eastern part of the sediment basin of the former Pannonian sea, which lay in the territory of central and the south-eastern Europe in the middle Miocene epoch, according to the findings of Nikic and Vidovic (24). As well as the high amount of NOM, the groundwater investigated also contains high amounts of arsenic (51.7 ± 16.4 μg As/L). The general characteristics of the groundwater are given in Table 2.

Experiments

Laboratory Scale Experiments

Laboratory experiments were performed with standard Jar tests as shown in the experimental scheme in Fig. 1.

Jar test experiments were performed using a FC6S Velp Scientific apparatus, with 0.6 L samples of already oxidized water in 1 L beakers at room temperature (22–25°C). A 10% working solution of $FeCl_3$ was prepared by diluting concentrated $FeCl_3$ of 187 g Fe/L. After coagulant addition, the water samples underwent fast mixing (120 rpm for 2 minutes), flocculation with addition of anionic flocculant A 110 of medium molecular weight (30 rpm for 30 minutes), and settling for 60 minutes. The flocculant dose used in this research was 0.5 mg/L. After clarification, the water samples were decanted and filtered through B1 Gooch filters. $FeCl_3$ was chosen as the coagulant for these investigations based on literature data (16), which shows that ferrous salts are very effective for the removal of high amounts of arsenic during the coagulation process.

The study was performed on water with pH correction (pH = 7.0 ± 0.1). Although it is well known that the optimal pH value for $FeCl_3$ application is around 5.0, the decision to perform the experiment at pH 7.0 was due to our primary concern in achieving a reduction of arsenic content below the required 10 μg/L. According to literature data (8), the optimal pH value for effective As removal by $FeCl_3$ is around 7.0. Also, reports from other authors (17) were taken into account, stating that it is expensive to adjust the pH to acidic conditions where the source water has high alkalinity (745 ± 12 mg $CaCO_3$/L, Table 2). Therefore, enhanced coagulation at acidic pH was deemed to be impractical.

Bench scale pre-oxidation of raw water was carried out in a glass tube (a continuous reactor with respect to ozone and discontinuous with respect to water). Ozone was generated by an Argentox ozonizer with a capacity of 20 g/h. The ozone doses used in the pre-oxidation process ranged between 2.5–12.8 mg O_3/L, which is 0.3–1.3 mg O_3/mg DOC. The O_3 and H_2O_2 doses applied in the O_3/H_2O_2 process gave the following $H_2O_2:O_3$ ratios: 0.7 (1.7 mg H_2O_2/L; 2.5 mg O_3/L), 0.6 (3.5 mg H_2O_2/L; 5.7 mg O_3/L), 0.3 (3.5 mg H_2O_2/L; 12.8 mg O_3/L) and 0.2 (1.7 mg H_2O_2/L; 7.0 mg O_3/L).

In the first series of the experiments, a wide range of 18–300 mg $FeCl_3$/L was used for the coagulation process in order to find the optimal dose of coagulant for effective As and NOM removal. The focus of the second series of

TABLE 2
Raw water quality characteristics

Parameter	Unit	Mean value ± sd	No. of measurements
pH	–	7.48 ± 0.14	n = 19
Turbidity	NTU	0.52 ± 0.03	n = 19
Total hardness	mg $CaCO_3$/L	745 ± 12	n = 19
El. conductivity	μS/cm	1202 ± 16	n = 19
DOC	mg C/L	9.27 ± 0.92	n = 8
UV_{254}	cm^{-1}	0.497 ± 0.015	n = 19
SUVA	$L\,mg^{-1}\,m^{-1}$	5.36 ± 0.49	n = 8
HCO_3^-	mg/L	909 ± 15	n = 19
Arsenic content	μg/L	51.7 ± 16.4	n = 19
THMFP	μg/L	536 ± 81.5	n = 8
HAAFP	μg/L	164 ± 5.6	n = 8
Aldehyde content	μg/L	14.7 ± 2.9	n = 8

sd–standard deviation.

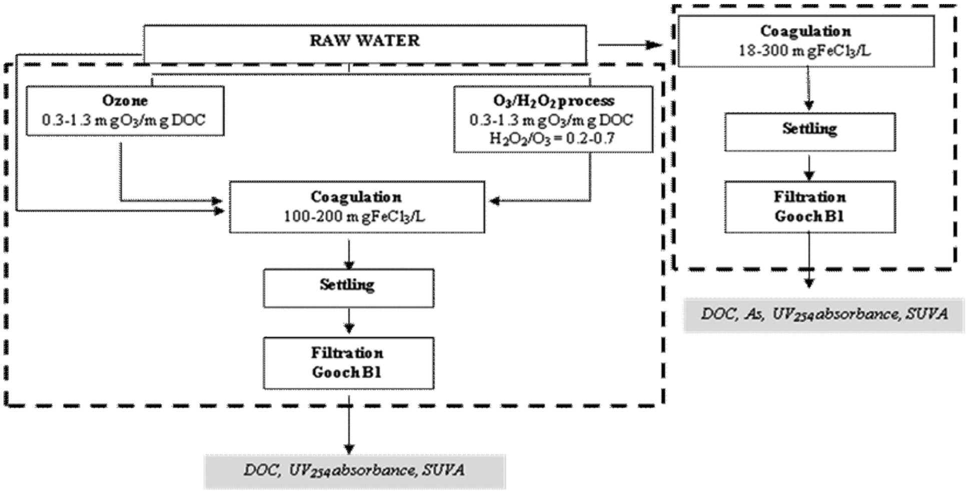

FIG. 1. Experimental scheme (bench-scale).

experiments was to investigate the possibilities of improving the coagulation process efficiency for NOM removal by applying a pre-oxidation process with O_3 and O_3/H_2O_2. In this series of experiments, a narrower range of coagulant dose of 100–200 mg $FeCl_3$/L was investigated.

Pilot Scale Experiments

The pilot plant used (capacity: 2 m^3/h) was designed to test various process trains consisting of a series of processes such as ozonation and O_3/H_2O_2, coagulation/sedimentation, and sand/anthracite filtration (SF) (Fig. 2).

The difference between the investigated treatment trains was in the applied oxidative pre-treatment: train A–ozonation (0.3 mg O_3/mg DOC) and train B - O_3/H_2O_2 process (0.3 mg O_3/mg DOC; $H_2O_2/O_3 = 0.6$). The coagulation reagent was ferrous chloride at a dose of 200 mg $FeCl_3$/L.

Analytical Methods

Water samples were analysed before and after coagulation for DOC content using a Thermo HiPerToc 2006.0167 after filtration through a 0.45 μm membrane filter (relative standard deviation, RSD ±2%). The method used was combustion at 1000°C. UV_{254} absorbance measurements were performed in accordance with standard methods (25) by UNICAM SP600 UV spectrophotometer at a wavelength of 254 nm with a 1 cm quartz cell (RSD ±2%). The specific UV absorbance (SUVA, $L\,mg^{-1}\,m^{-1}$) was calculated. pH and turbidity were measured by portable

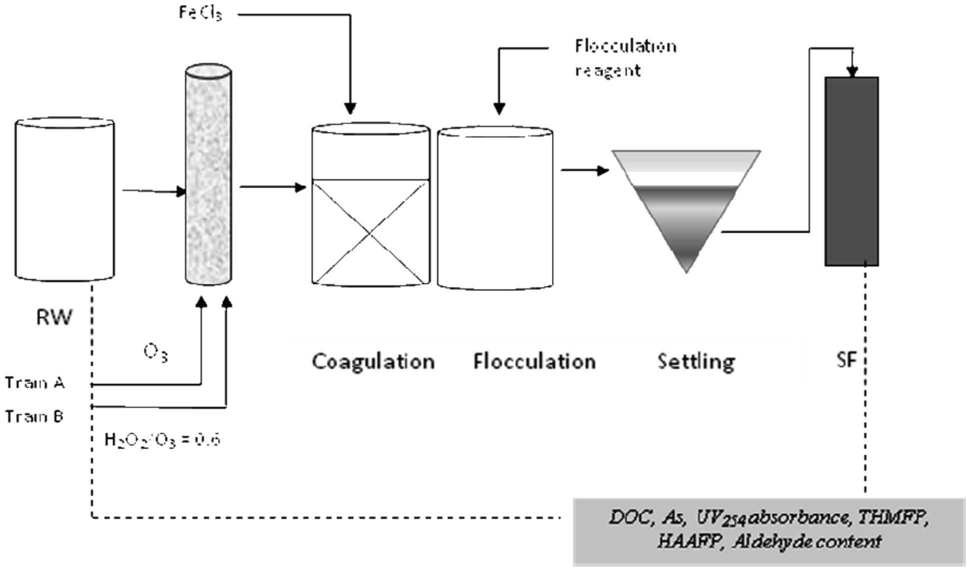

FIG. 2. Diagram of the pilot plant (RW: raw water; SF: water after coagulation/sedimentation/sand/anthracite-filtration).

instruments (WTW InoLab pH and Hanna HI 93703, RSD ±2%). The ozone content in the inlet and outlet gases was determined by iodometric procedure (25), and the ozone dose calculated from the difference. Arsenic characterization was carried out by fractionation on *Supelco* ENVI-18, LC-SAX, and LC-NH2 resins and analysis by Atomic Absorption Spectroscopy (Perkin Elmer AAnalyst 700) according to the method given by Yu et al. (26) (RSD ±5%). Trihalomethane formation potential (THMFP) and haloacetic acids formation potential (HAAFP) were determined according to a standard method for THMFP determination. Analysis of THMs and HAAs was performed by GC/μECD (Agilent 6890 N) (25,27). Aldehyde contents were determined by GC/MS (Agilent 7890A GC with 5975C MSD detector) after PFBHA derivatization in aqueous solution (25,28). The method detection limits (MDL) were determined from standard deviations of 0.2 μg/L for THM, 0.5 μg/L for HAA, and 1.0 μg/l for aldehydes. The corresponding MDLs for the THMs chloroform, BDCM, DBCM, and bromoform were 0.09, 0.01, 0.01, and 0.05 μg/L respectively. The corresponding MDLs for the HAAs MCAA, MBAA, DCAA, TCAA, BCAA, and DBAA were 0.03, 0.13, 0.54, 0.04, 0.25, and 0.05 μg/L respectively. The MDLs for formaldehyde, acetaldehyde, glyoxal, and methylglyoxal were 0.40, 0.16, 0.40, and 0.34 μg/L respectively.

RESULTS AND DISCUSSION

Two series of experiments were performed. The first series investigated the efficiency of the coagulation/flocculation process in NOM and As removal from groundwater with the application of $FeCl_3$ as a coagulant. The aim of this part of the experiment was to determine the possibilities of using $FeCl_3$ as a coagulant for As and NOM removal in water with high As and DOC contents. This is why a wide range of $FeCl_3$ doses (18–300 mg $FeCl_3$/L) was applied.

Effects of the Coagulation Process with $FeCl_3$ on NOM and As Reduction

Figure 3 shows the changes in As and NOM contents due to the coagulation process. Given the high amount of arsenic present in the raw groundwater (51.7 ± 16.4 μg As/L), which is several times higher than the MAL value of 10 μg/L required by Serbian legislation (5), the first focus of this experiment was to find an optimal coagulant dose to achieve this value. Given that the arsenic content in the raw groundwater could be up to 70 μg/L, to meet the required MAL value, the efficacy of the coagulation process for arsenic removal must be higher than 85%. The dominant species of As in the raw groundwater is As^{5+} (42%), followed by As^{3+} (35%) and organically bonded As (23%).

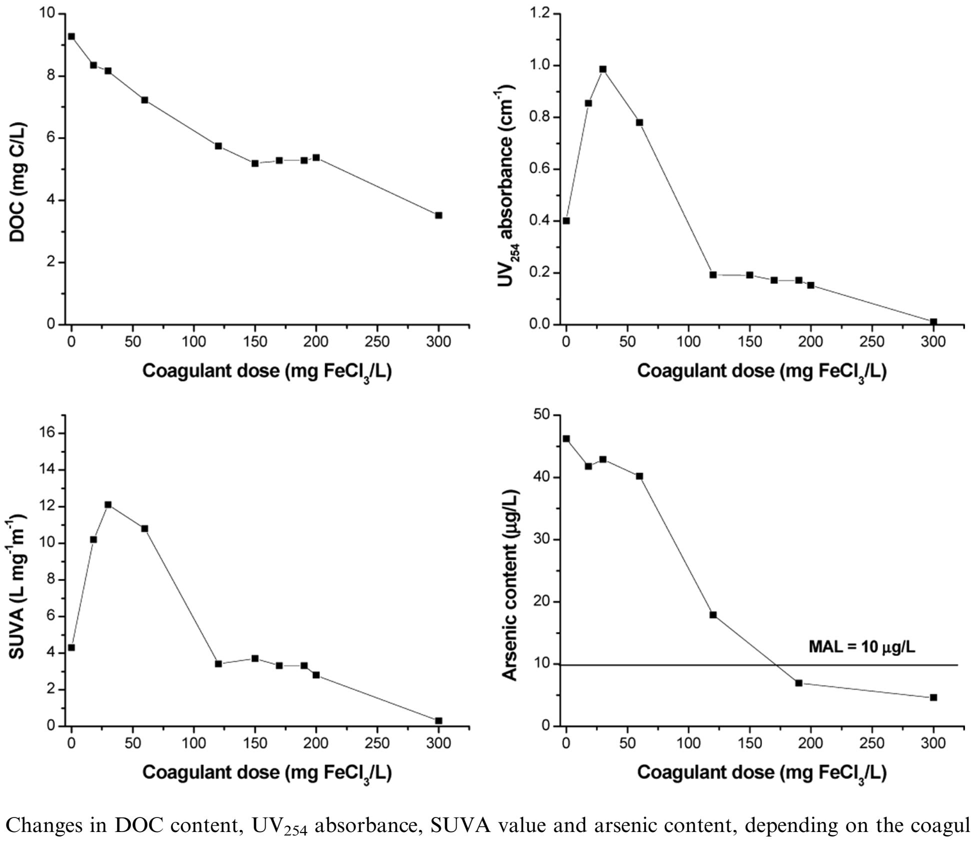

FIG. 3. Changes in DOC content, UV_{254} absorbance, SUVA value and arsenic content, depending on the coagulant dose.

The results show that the coagulation process alone, with $FeCl_3$ applied in doses of less than 100 mg/L, causes very low removal rates for As (up to 13%, relative to raw water), and for DOC (up to 22%). Also, the UV_{254} absorbance and thus the SUVA value increase relative to raw water with coagulant doses below 100 mg/L. This can be explained by poor settling in this range of coagulant concentrations, causing high turbidity and interfering with UV_{254} measurements.

More significant decreases in As (61–90%, relative to raw water) and DOC contents (38–62%) were observed for doses of coagulant higher than 100 mg $FeCl_3$/L. Applying 180 mg $FeCl_3$/L reduced the arsenic content to 6.96 µg/L, well below the required MAL of 10 µg/L. The coagulation process with this dose of $FeCl_3$ also decreased the DOC content by 43% relative to raw water, which is 30% more effective than that required for this type of water (TOC concentration higher than 8 mg/L and raw alkalinity over 120 mg $CaCO_3$/L) by USEPA D/DBP Rule (29). DOC reduction in these conditions was followed by significant hydrophobic fraction removal, as seen from UV_{254} absorbance and SUVA reductions of 57% and 25% respectively, relative to raw water.

As expected, these results show satisfactory performance of $FeCl_3$ (180 mg $FeCl_3$/L) as a coagulant at pH 7.0 ± 0.1 for arsenic removal. Some authors report that low doses of $FeCl_3$ (lower than 20 mg $FeCl_3$/L) used in the coagulation process are sufficient to remove high concentrations of As^{5+} (68 µg/L) from water, with over 90% efficacy (30). However, as can be seen from the results shown in Fig. 3, a much higher dose of 180 mg $FeCl_3$/L was necessary to achieve this removal efficacy. This could be a consequence of the high amount of As^{3+} present in the raw water, which cannot be removed efficiently by $FeCl_3$ (10). The need for a high coagulant dose can also be explained by the presence of a high amount of NOM in the raw water. Since one of the mechanisms of As removal by coagulation/flocculation is its adsorption on active sites of formed hydroxides, it can be assumed that NOM competes with arsenic for adsorption on flocs. This is also indicated in the research of Pallier et al. (10), who concluded that if such high amounts of NOM (DOC = 10 ± 0. 2 mg/L) are present, the coagulant dose needed for arsenic removal from 100 µg/l to 10 µg/L was much higher (about 100 mg $FeCl_3$/L) than the dose needed when arsenic was removed from water without NOM (around 50 mg $FeCl_3$/L). A coagulant dose of 180 mg $FeCl_3$/L showed high efficacy for DOC and UV_{254} absorbing material removal. However, after this treatment, the water still contained significant amounts of DOC (5.28 µg/L) due to very high amount of DOC in the raw groundwater (mean value 9.27 ± 0.92 mg/L). The DOC removal of 43%, relative to raw water, is similar to results obtained by Uyak and Toroz (7), with a high coagulant dose of 140 mg $FeCl_3$/L (40% removal).

Once the first series of experiments found the optimum $FeCl_3$ dose for satisfactory removal of As during coagulation, the focus of the second series of experiments was improving this process for NOM removal. To improve the performance of the coagulation process for NOM removal, different oxidation pre-treatments can be applied (21). The second series of experiments investigated the effects of two oxidation pre-treatments (ozone and O_3/H_2O_2 process) on the efficacy of the coagulation process for NOM removal, and arsenic removal was not followed, as it is known from the literature (4) that oxidation can only enhance the coagulation process efficacy by transforming As^{3+} into As^{5+}.

Effects of Ozone and O_3/H_2O_2 Process on DOC and UV_{254} Reduction during the Coagulation

The coagulant doses applied in the second set of laboratory tests were in a narrower range from 100–200 mg $FeCl_3$/L, where the most significant removal efficiency for NOM occurred according to the first series of experiments. This second series of experiments compared coagulation efficacy for NOM removal with and without the application of pre-oxidation processes. Figure 4 presents

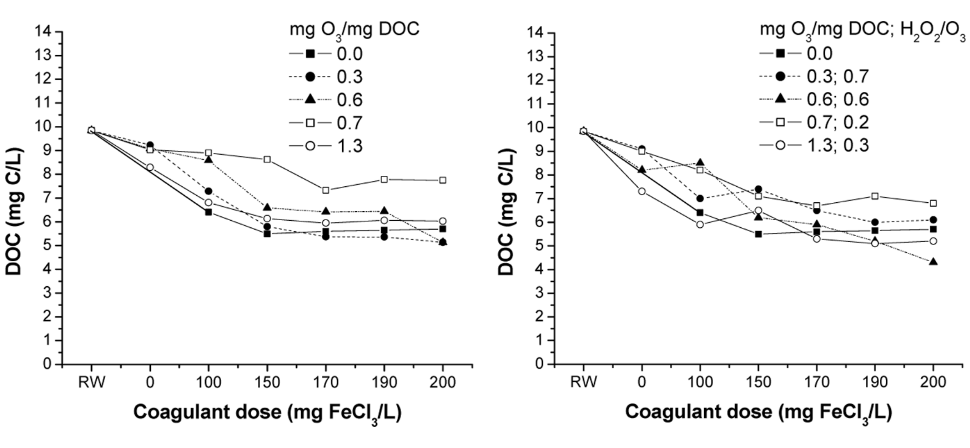

FIG. 4. Changes in DOC content depending on the applied oxidation reagent (ozone and O_3/H_2O_2 process) and coagulant dose (RW – raw water).

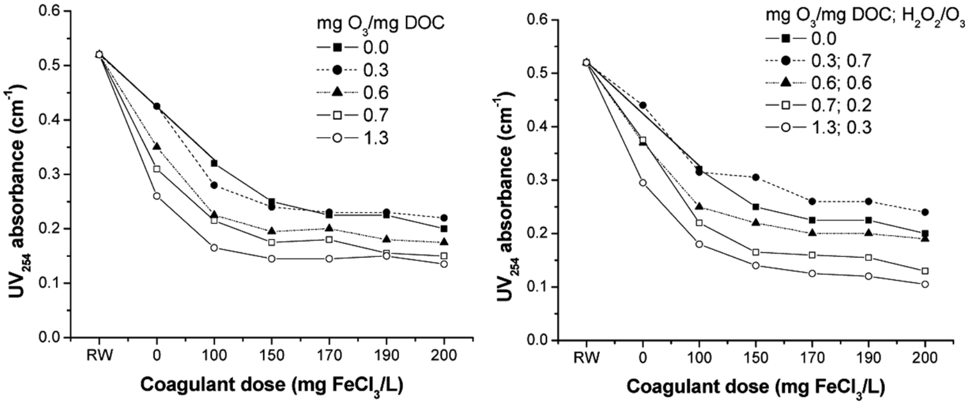

FIG. 5. Changes in UV_{254} absorbance depending on the applied oxidation reagent (ozone and O_3/H_2O_2 process) and coagulant dose (RW – raw water).

the results on the effect of ozone and O_3/H_2O_2 processes on DOC reduction during the coagulation process.

Relative to the DOC content of the raw water, the application of the coagulation process without pre-oxidation results in a DOC removal of 35–43%, using coagulant doses of 100–200 mg $FeCl_3$/L. The different oxidation processes showed different influences on coagulation process efficacy for DOC removal. Use of ozone as a pre-treatment only lead to a slight improvement of coagulation performance, and only in the case when the smallest investigated dose of 0.3 mg O_3/mg DOC was applied. A combination of this ozone dose with 200 mg $FeCl_3$/L during coagulation gave a reduction in average DOC from 9.27 mg C/L to 4.83 mg C/L (48% removal, relative to raw water). Increasing the ozone dose (>0.7 mg O_3/mg DOC) lead to coagulation process efficacy reduction, compared to the coagulation process alone.

Using the O_3/H_2O_2 process with a H_2O_2/O_3 ratio of 0.6 (0.6 mg O_3/mg DOC) and a coagulation dose of 200 mg $FeCl_3$/L, gave a DOC removal of 56% relative to raw water. The measured DOC value in this water was 4.3 mg C/L. From the results shown in Fig. 4, it can be concluded that the application of higher ozone doses in the O_3/H_2O_2 process (>0.7 mg O_3/mg DOC) did not contribute to better DOC removal, compared to the coagulation process alone, which is in agreement with the results obtained when ozone by itself was used as the oxidation reagent. The poor impact of higher doses of ozone and O_3/H_2O_2 on coagulation efficacy could be a consequence of greater oxidation of NOM and the formation of organic by-products with lower molecular weight, which have a low affinity to the hydrolysis products of $FeCl_3$, thus resulting in a reduction in organic matter removal efficacy, compared to the coagulation process alone (21,31).

Figure 5 presents the results of the effects of ozone and the O_3/H_2O_2 process on the coagulation process efficacy in reducing UV_{254} absorbing material.

Baseline coagulation decreases the UV_{254} absorbance value of the raw water by 38–62%. The highest removal was achieved using the highest applied dose of 200 mg $FeCl_3$/L. The results in Fig. 5 show that during the coagulation process, the UV_{254} absorbance decreased by 46 to 74% relative to raw water, with increasing ozone dose. This trend was also observed when higher doses of ozone (0.6 to 1.3 mg O_3/mg DOC) were applied with the O_3/H_2O_2 process as a pre-treatment, with a linear increase (from 52 to 82%, relative to raw water) of UV_{254} absorbance removal observed. This can be explained by the fact that the oxidation reagents react with double bonds, active aromatic constituents, and polar organic functional groups (21), which are known to induce high UV_{254} absorbance.

The results in Fig. 6 show the changes in SUVA value with increasing applied doses of ozone and O_3/H_2O_2 during the coagulation process.

These results indicate that increasing the coagulant dose during baseline coagulation leads to a linear decrease in the SUVA value of water (18–43% reduction relative to raw water), which can be attributed to the same trend as changes in the UV_{254} absorbance value. Generally, treatments in which an oxidation step is applied enabled an increase in coagulation process removal efficacy for the hydrophobic fraction of NOM (expressed as SUVA value), compared to coagulation/flocculation alone. The greatest SUVA value reductions of 49–64% relative to the raw water were obtained through application of oxidation pre-treatment with a H_2O_2/O_3 ratio of 0.2 (0.7 mg O_3/mg DOC) in combination with 100–200 mg $FeCl_3$/L in coagulation. Aromatic structures are important components of NOM with respect to DBP formation, because they are believed to constitute the primary sites attacked by chlorine or other oxidants. The decreases in SUVA, as a measure of NOM aromatic content, which were observed during the investigated treatments, indicate changes in the structure and removal of the hydrophobic aromatic fraction of NOM. Therefore, it can be assumed that although the investigated oxidation

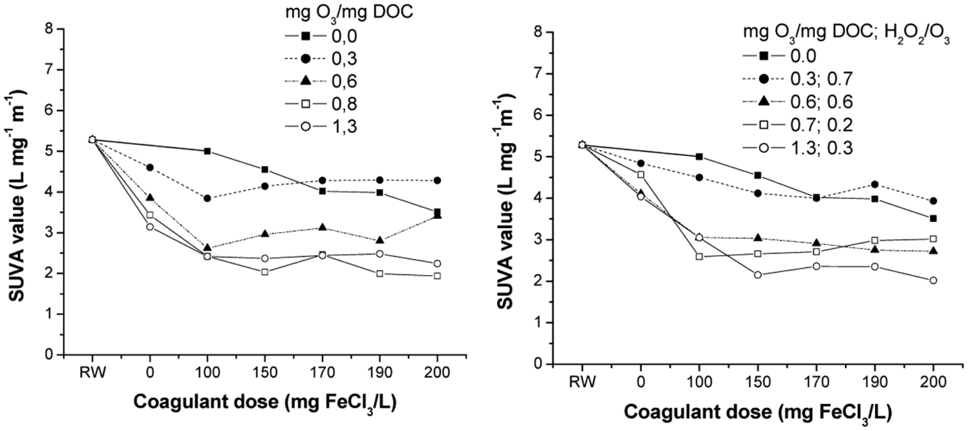

FIG. 6. Dependence of changes in the SUVA value on the applied oxidation reagent (ozone and O_3/H_2O_2 process) and coagulant dose (RW – raw water).

pre-treatments had a poor impact on the DOC removal achieved by the coagulation process, they can contribute to better removal of DBP precursors, which are one of the very important issues during drinking water treatment evaluation.

The results given in Figs. 4, 5, and 6 are in agreement with observations of other authors (32), who suggest that the application of ozone and the O_3/H_2O_2 process can contribute to structural changes in the NOM present in water. This statement is confirmed by the good reduction of UV_{254} absorbance and SUVA value with increasing O_3 and O_3/H_2O_2 dose. However, increasing the oxidant dose during pre-treatment, although strongly effecting the content of UV_{254} absorbing material, does not have a significant influence on DOC removal by coagulation/flocculation, which confirms the conclusions by other researchers that oxidation pre-treatment does not necessarily lead to an increase in coagulation process efficacy for overall DOC content removal, compared to the coagulation process by itself (21).

In order to evaluate the results obtained during the laboratory tests under more realistic treatment conditions, pilot plant tests were conducted.

Pilot Plant Experiments

The following doses of oxidation reagents (O_3 and O_3/H_2O_2) were applied in the pilot plant tests in combination with a coagulant dose of 200 mg $FeCl_3$/L:

- for ozone pre-treatment - 0.3 mg O_3/mg DOC (Train A),
- for H_2O_2/O_3 process - 0.3 mg O_3/mg DOC, $H_2O_2/O_3 = 0.6$ (Train B),

The dose of 0.3 mg O_3/mg DOC was chosen as this dose in combination with 200 mg $FeCl_3$/L gave the highest reduction of DOC in the laboratory tests, and DOC is the main parameter concerning NOM content in water. Meanwhile, for the combined oxidation reagent, a ratio of $H_2O_2/O_3 = 0.6$ gave the best DOC removal, and so this was also applied during the pilot plant investigations.

Treatment efficacy was evaluated on the basis of DOC content, UV_{254} absorbance, THMFP, HAAFP, aldehydes content, and arsenic content. The results are given in Table 3. Table 4 presents the average formation potential values for each THM (chloroform; BDCM; DBCM;

TABLE 3
NOM and arsenic contents in raw and treated water

Treatment train	DOC ± sd (mg C/L)	UV_{254} ± sd (cm^{-1})	THMFP ± sd (μg/L)	HAAFP ± sd (μg/L)	Aldehydes ± sd (μg/L)	Arsenic ± sd (μg/L)
Raw water[a]	9.27 ± 0.92	0.497 ± 0.02	536 ± 81.5	164 ± 5.6	14.7 ± 2.9	51.7 ± 16.4
			Train A			
water after SF[b]	3.80 ± 0.64	0.149 ± 0.01	251 ± 19.8	50.0 ± 7.8	18.0 ± 2.1	1.55 ± 0.5
			Train B			
water after SF[b]	2.50 ± 0.17	0.106 ± 0.006	210 ± 32.0	66.4 ± 9.5	11.9 ± 3.8	1.03 ± 0.7

[a] sd–standard deviation from 8 measurements.

[b] sd–standard deviation from 3 measurements.

TABLE 4
Average potential formation value of each THM and HAA, and aldehydes content in the raw and treated water

Treatment train	THMFP (μg/L)				HAAFP (μg/L)						Aldehydes (μg/L)			
	Chloroform	BDCM	DBCM	Bromoform	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	Formaldeyde	Acetaldehyde	Glyoxal	Methylglyoxal
Raw water	486	46.4	3.4	<MDL	5.1	62.7	2.9	87.6	5.6	0.2	12.4	2.2	<MDL	<MDL
Train A														
water after SF	197	57.4	12.5	0.5	5.8	18.3	2.4	14.8	7.8	0.9	10.1	1.6	4.0	2.4
Train B														
water after SF	150	56.9	13.6	0.7	8.9	25.5	4.9	17.1	8.0	2.0	4.9	2.0	3.9	0.7

bromoform) and HAA (MCAA; MBAA; DCAA; TCAA; BCAA; DBAA), as well as the aldehydes content (formaldehyde, acetaldehyde, glyoxal, and methylglyoxal) in the raw and treated water.

The results presented in Table 3 show that arsenic removal efficacy is much higher (above 97%, relative to raw water) in the investigated treatment trains than the coagulation process alone, which achieved an 85% reduction during the laboratory tests. This removal rate is sufficient to ensure good quality water with respect to As content. The increased As removal efficiency by coagulation can be explained by oxidation during pre-treatment of As^{3+} in the raw water into As^{5+}, which is more easily removed by $FeCl_3$ coagulation, according to the literature (8).

Concerning NOM content, the pilot plant results confirmed expectations based on laboratory test results. With the same dose of ozone applied in both treatment trains, O_3/H_2O_2 enabled better DOC removal efficacy by coagulation, resulting in 2.50 ± 0.17 mg/L in treated water. Similar removal efficacies for UV_{254} absorbing material (about 70% removal relative to raw water) were achieved by both treatment trains. Since the ozone dose was also the same in both investigated treatment trains, it can be assumed that changes in UV_{254} absorbing material is mostly dependent on the applied ozone dose.

The formation potentials of THM and HAA indicate that both treatment trains effectively reduce the NOM fractions which represent their precursors.

From the results presented in Table 4, it can be seen that chloroform precursors contribute a major part to the total THM formation potential in raw water (average 486 μg/L). The average BDCMFP for raw water is 46.4 μg/L and DBCMFP 3.4 μg/L. Bromoform precursors were not detected in the raw groundwater. Chloroform formation potential decreases in the investigated treatment trains, while brominated THM formation potential increases after oxidation pre-treatment and the coagulation/sedimentation/SF process, in comparison with raw water values. However, because of the lower values for formation potential of BDCM, DBCM, and bromoform, the total THMFP follows the chloroform potential formation trend and decreases along the treatment trains (Table 3). The percentage removals of THMFP after the investigated treatment trains were similar (a decrease of 53–61%, relative to the raw water). However, after both trains, the water still contained significant amounts of THM precursors (above 200 μg/L).

TCAA and MBAA precursors are the major contributors to the total HAA formation potential of raw water, with average formation potentials of 87.6 μg/L and 62.7 μg/L, respectively. The formation potentials for MCAA, DCAA, BCAA, and DBAA in raw water were all below 6.0 μg/L. After the coagulation/sedimentation/SF process in the investigated treatment trains, a decrease in the formation potential of MCAA, MBAA, DCAA, TCAA, and BCAA is observed, relative to the raw water. An exception is DBAA, the precursors' content of which constantly increases after the investigated treatment trains, which is in agreement with the trends for dibrominated (DBCM) and tribrominated (bromoform) THMs. The influence of ozone and O_3/H_2O_2 on total HAA formation potential after the coagulation/sedimentation/SF is similar (a decrease of 60–69%, relative to the raw water).

HAA formation potentials for coagulated water (after Train A – 50.0 ± 7.8 μg/L and Train B – 66.4 ± 9.5 μg/L) show that less of their precursors remain after the investigated treatments than the THM precursors. It is reasonable to assume that in real disinfection conditions (which apply a lower chlorine dose than the potential formation determination procedure) the amount of HAA formed would probably be below the MAL values given by Serbian legislation (50 μg/L for DCAA).

Aldehydes are known oxidation by-products of ozone and related oxidation reagents (13). As the results show (Table 4), only formaldehyde and acetaldehyde were detected in the raw groundwater. Aldehydes were detected also in the coagulated water, but for both treatment trains, only in amounts (Train A – 18.0 ± 2.1 μg/L and Train B – 11.9 ± 3.8 μg/L) of a similar magnitude to the amounts detected in the raw groundwater (14.7 ± 2.9 μg/L).

Sludge obtained in the pilot plant after settling during the investigated treatment trains contained a high amount of arsenic (average of 600 mg/kg). This concentration is much higher than the allowed concentration of arsenic (41 mg/kg) for safe disposal, according to USEPA 40 CFR 503 (33). The possibilities of flocculation sludge stabilization and disposal will be the subject of further investigations which will offer a suitable solution in accordance with environmental protection requirements.

CONCLUSIONS

This article investigates the effect of the coagulation process with $FeCl_3$ on arsenic and natural organic matter removal from groundwater. In laboratory- and pilot-scale tests, a comparison of two oxidation pre-treatments (ozone and O_3/H_2O_2 process) was made, using groundwater which contains high amounts of arsenic and NOM. The results obtained indicate that:

- coagulation with 100–200 mg $FeCl_3$/L shows high efficacy for arsenic removal (up to 85%, relative to raw water) at pH 7.0, but with much lower NOM content reduction (DOC reduction of 43%), probably due to unfavorable pH conditions.
- 0.3 mg O_3/mg DOC, applied as ozone alone and in the O_3/H_2O_2 process ($H_2O_2/O_3 = 0.6$) has a comparable influence on the coagulation process

in terms of improved As reduction. Coagulation with 200 mg $FeCl_3$/L in combination with each oxidation reagent enabled arsenic content removal to below 2 μg/L, which is lower than MAL value of 10 μg/L by Serbian legislation.

- Laboratory tests have shown that application of ozone during pre-treatment has a lower influence on coagulation efficacy in terms of DOC reduction, compared to the O_3/H_2O_2 process with the same ozone dose. These results were confirmed at the pilot plant—the coagulated water after Train A (ozone) contained 3.80 ± 0.64 mg C/L, and after Train B (O_3/H_2O_2), 2.50 ± 0.17 mg C/L.
- Based on UV_{254} and SUVA value changes, it can be concluded that increasing the ozone dose in both oxidation reagents leads to increased removal hydrophobic and aromatic material during the coagulation process. However, higher H_2O_2/O_3 ranges showed a negative impact on UV_{254} measurements.
- The two oxidation pre-treatments showed similar effects on coagulation efficiency for THM and HAA precursor removal. Aldehydes, which are known oxidation by-products of ozone and related oxidation reagents, were only detected in the coagulated water in small amounts (less than 20 μg/L).

These experiments were conduced as part of wider investigations into different possibilities for NOM and arsenic removal from groundwater. Further research in this field is planned on the basis of the positive results obtained in this investigation.

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