Pilot scale investigation of coagulation combined with ozonation and pH adjustment in treatment of NOM rich water


ABSTRACT

This paper presents the results of a pilot scale investigation of coagulation using aluminium based coagulants (polyaluminium chloride sulphate (PACL1) and polyaluminium chloride (PACL2)), combined with pre-ozonation and pH adjustment, on natural organic matter (NOM) removal from groundwater. Tests were conducted at a semi-industrial pilot plant, using groundwater with a high content of NOM (5.1 ± 0.8 mg C/L dissolved organic carbon (DOC); 0.211 ± 0.007 cm⁻¹ UV absorbance at 254 nm (UV254)). It was determined that both coagulants showed similar efficacy in reducing DOC (∼50%), UV254 (∼60%) and THMFP (∼65%). Application of pre-ozonation enhanced total coagulation efficiency (up to 61% and 80% for DOC and UV254, respectively), probably due to its microflocculation effect. THMFP in the treated water fluctuated depending on ozone dose, coagulant type and pH. The pre-treatment resulted in NOM oxidation to lower molecular weight hydrophilic organic substances. PACL1 coagulation did not efficiently remove these new THM precursors, whereas PACL2 was able to reduce THMFP to 77 μg/L at a low ozone dose of 0.4 mg O₃/mg DOC, suggesting differences in the coagulation mechanism for the two coagulants. This difference confirms the necessity of optimizing the combined treatment depending upon the choice of coagulant applied.

Key words | coagulation, natural organic matter, ozonation, pH adjustment, pilot plant

INTRODUCTION

The presence of natural organic matter (NOM) has a negative impact on the quality of drinking water from several aspects. One of the most important is the undesirable formation of disinfection by-products (DBPs), many of which are toxic (Matilainen et al. 2010; WHO 2011; Gonsior et al. 2014). In order to create a balance between the risk of microbiological and chronic chemical contamination of drinking water, the most widely used treatment option is the disinfection using chlorination, carried out after NOM removal. Conventional drinking water treatment consists of coagulation/flocculation, sedimentation and filtration, and is commonly applied to remove NOM (>35%) and control DBPs formation (Yan et al. 2008a). The main mechanism for removing NOM by coagulation is neutralizing the charge of colloidal NOM, precipitation and adsorption to the co-precipitate metal hydroxides (Uyak & Toroz 2007; Matilainen et al. 2010). The degree of NOM removal depends on their characteristics and the coagulation conditions. According to the literature, the reduction of total trihalomethane formation potential (THMFP) in natural and synthetic waters can be in the range 17–89% (Li et al. 2015). Good practice for improving the coagulation process includes the introduction of enhanced coagulation in order to reduce the extent to which people are exposed to DBPs. Enhanced coagulation is defined as a process that allows a higher degree of NOM removal compared to the conventional treatment, as a result of optimizing the dose, the type of coagulant and the pH during coagulation (Yan et al. 2008a). Coagulants based on...
a new generation of polyaluminium chloride (PACL) are widely used in the treatment of drinking water (Matilainen et al. 2010; Li et al. 2015). Conventional coagulants must first be hydrolyzed to form active positively charged particles. However, PACL coagulants are solutions with pre-formed polymer particles of aluminium. PACL is one of the most important polymers used in the treatment of drinking water, usually at doses ranging from 0.02 to 0.24 mmol Al/L (Yan et al. 2008b). PACL are stable over a wide pH range and have open structures with large surfaces full of available sites for adsorption and complexation of NOM molecules. These coagulants can be prepared to suit the specific characteristics of particular raw waters. pH control of the water is very important to optimize the coagulation process, as changes to the pH may result in the reduction of the charge density of the NOM, making them more hydrophobic (absorbable) (Uyak & Toroz 2007; Matilainen et al. 2010). To improve the effects of the coagulation process in the removal of the NOM and control of the DBP formation, particularly in water with a high content of these materials, oxidative pre-treatment by ozone is increasingly being applied prior to the coagulation process. It is known that the process of pre-ozonation has a positive effect on the removal of NOM from water, within a relatively narrow range of ozone doses (0.4–0.8 mg O₃/mg TOC), especially on the part which is a precursor material for DBPs (Liu et al. 2009; Tubić et al. 2011; Sadrnourmohamadi & Gorczyca 2015). It is therefore necessary to examine and define optimal conditions of oxidative treatment and coagulation for each type of water, in order to efficiently remove NOM from water. It should also be noted that results obtained under laboratory conditions are not always easy to achieve in large scale water treatment plants. Therefore, the aim of this work was to conduct a pilot scale investigation into the influence of pre-ozonation with and without pH adjustment on coagulation efficiency for the treatment of groundwater rich in NOM.

**MATERIALS AND METHODS**

**Pilot scale water treatment**

The experiments were conducted on a pilot plant (capacity 2 m³/h) in order to optimize the drinking water treatment technologies, which included coagulation and coagulation enhanced with pH adjustment and pre-ozonation, sedimentation and filtration on dual media filters. During the optimization of the removal of NOM by coagulation, water samples were analyzed for dissolved organic carbon (DOC), UV absorbance at 254 nm (UV₂₅₄), specific UV absorbance (SUVA) and THMFP. Changes in the total aldehydes contents, as typical ozone oxidation products, were also measured relative to the raw water. Coagulation/flocculation of the raw water and the water after pre-ozonation (with and without prior pH adjustment) was carried out using polyaluminium chloride sulphate (PACL1) and polyaluminium chloride (PACL2) with doses of 10 g Al/m³. The main characteristics which differentiate the investigated coagulants are: PACL1 has an Al₂O₃ content of 9 ± 1%, Cl content of 7 ± 1% and a SO₄²⁻ content of 4 ± 1%, whereas PACL2 has an Al₂O₃ content of 18.9 ± 1.0% and a Cl content of 6.2 ± 0.5%. The coagulation doses applied at the pilot plant were chosen based on results obtained from a previous laboratory investigation (using the standard jar test procedure; results not presented), and are in the range of commonly used doses according to the literature (Yan et al. 2008b; Amin et al. 2012; Lou et al. 2012). After coagulant addition, water underwent fast mixing (180 rpm/min) for 1–2 min., followed by addition of flocculant in continual slow stirring mode (22 rpm/min) for 20 min. The majority of flocules were removed by sedimentation (retention time of 75 min), and the remaining flocules were removed by filtration in dual media filters (sand filter with a grit of 0.7–1.2 mm and an anthracite filter with granulation of 0.8–1.6 mm) at a filtration rate of 6–9 m³/h. Pre-ozonation of the raw water was carried out in an ozone contactor with a height of 6 m. Ozone was generated using an ozone generator with a capacity of 20 g O₃/h and was fed into the water injector. The applied ozone doses were 0.6–4.0 g O₃/m³ (0.1–0.8 mg O₃/mg DOC). Raw water pH adjustment was carried out in a separate 100 L reservoir by pulsed dosing of hydrochloric acid (5% v/v), which then flowed to the coagulation pool, or pre-ozonation column, depending on the treatment investigated.

**Analytical methods**

Water samples were analyzed for DOC content by ANATOC Analyzer, SGE, after filtration through a
0.45 μm membrane filter, in accordance with Method SRPS ISO 8245:2007 (SRPS ISO 2007). The practical quantification level for DOC analysis was 0.5 mg C/L. UV<sub>254</sub> absorbance measurements were performed in accordance with Standard Methods (AWWA-APHA-WEF 2012) on a UNICAM SP600 UV spectrophotometer with a 1 cm quartz cell at a wavelength of 254 nm. SUVA (Lmg<sup>-1</sup> m<sup>-1</sup>) was calculated (UV<sub>254</sub>/DOC<sup>*</sup>100). pH was measured by portable instrument (WTW InoLab pH). Determination of active chlorine in a sodium hypochlorite solution applied for water disinfection was performed using the standard iodometric procedure (AWWA-APHA-WEF Standard Methods 2012). Chlorine demand was determined in accordance with Standard Methods (AWWA-APHA-WEF 2012). The concentration of ozone in the inlet and outlet gas was determined by iodometric procedure (AWWA-APHA-WEF 2012), and the applied ozone dose was calculated on the basis of their difference. Complete ozone consumption was confirmed by measuring the residual ozone in the water using potassium indigotrisulfonate, according to Standard Methods (AWWA-APHA-WEF 2012). THMFP was determined according to Standard Methods (AWWA-APHA-WEF 2012). At the end of the 7 day reaction period, the samples were dechlorinated, and THMs were analyzed. THM (chloroform, bromodichloromethane – BDCM, dibromo-chloromethane – DBCM, and bromoform) formation in the water samples was analyzed by gas chromatograph equipped with mass selective detector, GC/MSD (Hewlett Packard 5890 GC, SERIES II/5971 MS), after liquid–liquid extraction. The accuracy of the THM measurements was determined using 15 spiked distilled water samples with THM mixture in concentration of 7.0 μg/L, and was 151 ± 6.6% for chloroform, 100 ± 6.4% for BDCM, 91.4 ± 7.5% for DBCM and 87.0 ± 8.4% for bromoform. Aldehyde contents (formaldehyde, acetaldehyde, glyoxal and methylglyoxal) were analyzed by GC/MSD (Hewlett Packard 5890 GC SERIES II/5971 MS), after liquid–liquid extraction and derivatization using PFBHA (O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride) in accordance with the method proposed by Glaze et al. (1989). Mean recovery values for the investigated aldehydes (based on measurement of 10 samples enriched with 15.4 μg/L formaldehyde, 15.0 μg/L acetaldehyde, 19.8 μg/L glyoxal and 18.1 μg/L methylglyoxal) were 107.3 ± 5.7% for formaldehyde, 96.8 ± 11.2% for acetaldehyde, 94.4 ± 7.4% for glyoxal and 96.6 ± 8.3% for methylglyoxal.

RESULTS AND DISCUSSION

Raw groundwater characteristics

The groundwater used for the experiments originates from Northern Banat, Republic of Serbia (well depth 180–220 m). The characteristics of the raw water are given in Table 1, based on 200 samples analyzed over a period of 1 year. Usual water supply practice in the local waterworks is to mix groundwater from different wells of varying quality, and to vary the degree of exploitation in the wells utilized over time. Relatively large variations in the water quality are therefore observed.

The organic parameters have high values, and indirectly show that the investigated groundwater is very rich in NOM (Table 1). The DOC value of 5.1 ± 0.8 mg C/L is much higher than the usually reported values in groundwaters (0.6–2.9 mg C/L) used as drinking water sources (Huang et al. 2004; Jarvie et al. 2005). Furthermore, the UV<sub>254</sub> absorbance (0.211 ± 0.007 cm<sup>-1</sup>) and the high SUVA value, in range of 3.9–4.7 L mg<sup>-1</sup> m<sup>-1</sup>, indicate that the NOM present in the water is predominantly hydrophobic in nature, and that significant amount of the NOM can therefore be removed by the coagulation process (Edzwald 1993). As expected, the total aldehydes content in raw water was not high (2.51 ± 1.80 μg/L). On the other hand, the high amount of NOM in water resulted in a high THMFP value (273 ± 73 μg/L), which is the most commonly used surrogate parameter for all other possible toxic chlorine DBPs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Mean value ± sd</th>
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<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>8.19 ± 0.16</td>
</tr>
<tr>
<td>DOC</td>
<td>mg C/L</td>
<td>5.1 ± 0.8</td>
</tr>
<tr>
<td>UV&lt;sub&gt;254&lt;/sub&gt;</td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.211 ± 0.007</td>
</tr>
<tr>
<td>THMFP</td>
<td>μg/L</td>
<td>273 ± 73</td>
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<tr>
<td>Total aldehydes</td>
<td>μg/L</td>
<td>2.51 ± 1.80</td>
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sd, standard deviation.
The influence of coagulation on NOM and THM precursors removal from the water

The effects of coagulation with polyaluminium based coagulants (PACL1 and PACL2) on changes in the NOM content in the investigated water are presented in Table 2.

The results indicate that both investigated coagulants showed similar high efficiency in NOM removal (removing ~50% of DOC and ~60% of UV254 absorbance), predominantly aromatic structures. The NOM removal results are reflected in the high removals of THM precursors achieved by coagulation (65%, relative to raw water), with the THMFP values after coagulation with either coagulant being almost the same. Comparing the degree of reduction of NOM surrogate parameters, one can conclude that the coagulation treatment with both polyaluminium based coagulants is 1.14 to 1.30 times more effective in removing UV254 absorbance in relation to the removal of DOC, which is consistent with observations made by other authors (Musikavong et al. 2005; Uyak & Toroz 2007).

Influence of pre-ozonation on NOM removal and DBP formation in coagulated water

In order to improve the effects of coagulation, the raw water was subjected to oxidative pre-treatment with ozone (Figure 1).

Many researchers suggested that ozone causes significant structural changes in NOM, such as pronounced and rapid reduction of colour and UV254 absorbance, the reduction of molecular weight, an increase of the content of low molecular weight compounds, biodegradability and polarity of organic compounds, etc. Ozone also contributes to better removal of NOM by coagulation due to its microfloculation effect (Agbaba et al. 2004; Bose & Reckhow 2007; Zhang et al. 2008; Molnar et al. 2013). However, Xing et al. (2012) suggested that the hydrophilic fraction of NOM is difficult to remove and lags in the coagulated water. That is why it is necessary to optimize the conditions of ozone pre-treatment applied in order to change the NOM structure. Our findings are consistent with the aforementioned effects of ozone, indicating a positive effect of pre-ozonation on reduction of DOC and UV254 absorbance in coagulated water. Depending on the ozone dose (0.1–0.8 mg O3/mg DOC) in the pre-treatment and after the process of coagulation with PACL1 and PACL2, DOC content was lower by 51–53% and 55–61%, and UV254 absorbance by 67–76% and 63–80%, respectively, relative to the raw water. Thus, pre-ozonation resulted in slightly improved coagulation efficacy for DOC removal and more significantly for UV254, where maximum efficacy was achieved using 0.8 mg O3/mg DOC. Based on the SUVA value (<3.0 Lmg⁻¹m⁻¹), at lower doses of ozone (0.1–0.2 mg O3/mg DOC) after coagulation with PACL1, hydrophobic and hydrophilic NOM components remained in

(Gonsior et al. 2014). All of this indicates the necessity of the chemical treatment of the investigated groundwater.

| Table 2 | Average NOM and THM precursors removal by polyaluminium based coagulants |
| Coagulant applied | Dose (g Al/m³) | pH | DOC (mg C/L) | UV254 (cm⁻¹) | SUVA (Lmg⁻¹m⁻¹) | THMFP (μg/L) |
| PACL1 | 10 | 7.74 ± 0.15 | 2.7 ± 0.42 | 0.082 ± 0.003 | 3.04 ± 0.007 | 94 ± 19 |
| PACL2 | 10 | 7.96 ± 0.16 | 2.5 ± 0.39 | 0.088 ± 0.003 | 3.52 ± 0.006 | 96 ± 20 |
the water, upon which coagulation has a low effect. In contrast, in the water after coagulation with PACL2 and pre-ozonation with ≥0.4 mg O₃/mg DOC, the SUVA fell below 3 Lmg⁻¹m⁻¹. In other words, PACL1 showed a higher affinity for hydrophobic NOM with higher molecular weight. Chow et al. (2009) have shown that coagulation depends on the characteristics of the DOC, and that the residual DOC after treatment is characterized by the presence of lower molecular weight components and lower SUVA values compared with the raw water, which is in agreement with the results of this study.

The results showing the influence of ozone dose on THMFP and aldehydes content in coagulated water are presented in Figure 2.

Coagulants PACL1 and PACL2 showed the same efficacy in reducing the THM precursors content by 66% and 65%, respectively, relative to the raw water, which is consistent with literature data (Uyak & Toroz 2007; Chiang et al. 2009). However, after introducing the oxidative pre-treatment, a significant difference in the efficacy of the THMFP removing process was observed. Thus, the combined treatment resulted in an overall reduction in THMFP of 41–54% (PACL1) and 49–72% (PACL2), relative to the raw water. The THMFP in coagulated water fluctuates depending on the applied ozone dose, and only improved coagulation efficacy at 0.4 mg O₃/mg DOC combined with PACL2 (around 20% reduction). The lower level of THM precursor removal can be explained by the structural changes of NOM during oxidation, primarily in terms of their polarity, which contributes to lower reduction of these compounds during coagulation. In addition, a significant role is played by the fact that during the process of pre-ozonation there is the formation of new organic compounds, especially aldehydes and hydroxylated aromatic compounds that give m-dihydroxy aromatic derivatives, known precursors of THM (Kleiser & Frimmel 2000). The water after coagulation (especially with PACL1) contained residual hydrophilic organic substances of lower molecular weight (SUVA < 3 Lmg⁻¹m⁻¹), which according to Kitis et al. (2001), are responsible for the formation of THM. In accordance with this, in water which is treated with PACL1 under all ozone doses investigated, a larger amount of THM precursor material (THMFP = 125–162 μg/L) remains than is the case with water coagulated with PACL2 (THMFP = 77–138 μg/L). As expected, the total aldehydes content increased when the ozone pre-treatment was used, but after coagulation (PACL1 and PACL2) the total aldehyde content did not exceed a concentration of 10 μg/L. The most abundant aldehydes were formaldehyde and glyoxal at concentrations of up to 4 μg/L.

The effect of pH adjustment on the NOM removal and DBP formation in the water treated by pre-ozonation and coagulation

Figure 3 presents the results of the pH adjustment on the removal of NOM and THM precursors by pre-ozonation and coagulation, as well as on aldehydes formation.

A large number of studies show that determining the optimum pH of coagulation is of great importance to achieve the most efficient removal of organic precursors from the water (Uyak & Toroz 2007; Matilainen et al. 2010). pH is also one of the most important process parameters for ozonation, determining to what extent the mechanisms of oxidation of organic matter by ozone will be represented (Von Sonntag & von Gunten 2012). To investigate the possibility of reducing the applied ozone dose without decreasing the efficacy, adjustment of raw water pH was carried out from 8.19 to 6.8, the lowest limit for drinking water according to the Serbian drinking water...
Under the given conditions, after pre-treatment with coagulant PACL1, organic matter contents were 53% lower for DOC and 79% for UV$_{254}$ absorbance, relative to the raw water. Application of pH adjustment did not improve the DOC removal by enhanced coagulation process, but the final contents of UV$_{254}$ absorbing organic matter and THM precursors were 14% and 35% lower, respectively, in relation to the same treatment without pH adjustment. This improvement can be explained partly by selective oxidation of NOM by predominantly molecular ozone, whose stability in water increases with decreasing pH value (Von Sonntag & von Gunten 2012).

The use of pH adjustment prior to the application of pre-ozonation and coagulation with PACL2 was less effective. The DOC values indicate a slightly lower level of NOM removal, which are reflected by the THMFP values (increased by 1.2 times). At the same time, the observed decrease in UV$_{254}$ absorbing compounds indicates that there has been a change in the NOM structure, which seems to correspond with the increase in the fraction contributing to THM formation. Whereas pH adjustment did not generally improve the PACL2 combined treatment process, the process with PACL1 was improved sufficiently to justify the use of a lower ozone dose. When compared with the combined treatment which applied the maximum ozone dose (0.8 mg O$_3$/mg DOC), the treatment with pH adjustment and an ozone dose of 0.4 mg O$_3$/mg DOC achieved very comparable removals of DOC and UV$_{254}$ absorbance, and achieved significantly better THMFP removal.

In addition, the total aldehydes content was almost two times lower after pre-ozonation and coagulation with pH adjustment compared with the same process without pH adjustment (Figure 3). Although the aldehyde contents in the treated waters investigated are not high, this observation could be useful for the treatment of waters in which higher amounts of aldehydes are formed in reaction with ozone.

**CONCLUSIONS**

The paper studies the effect of pre-ozonation on coagulation with polyaluminium based coagulants at different pH on the removal of NOM as THM precursors. Results from the drinking water pilot plant show that the coagulants have similar efficacy for total NOM removal when they are used alone or combined with ozone oxidation pre-treatment. Pre-ozonation resulted in slightly improved coagulation efficacy for DOC removal and more significantly for UV$_{254}$, where maximum efficacy was achieved using 0.8 mg O$_3$/mg DOC. During the combined treatment with pre-ozonation and pH adjustment (to pH 6.8), pH adjustment did not generally improve the PACL1 combined treatment process, but the process with PACL2 was improved such that even a lower ozone dose (0.4 mg O$_3$/mg DOC) resulted in a
lower level of residual THM precursors. The significant difference between the two coagulants confirms the necessity of optimizing the combined treatment depending upon the choice of coagulant applied.

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REFERENCES


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