Improving natural organic matter and turbidity removal from surface water by pre-coagulation combined with ozone/ultrasound
Parastoo Setareh, Meghdad Pirsaheb, Seyed Mostafa Khezri and Hiwa Hossaini

ABSTRACT
Recently, we showed that pre-treatment with ultrasound/ozone (US/O₃) could remarkably enhance the performance of coagulation in removing natural organic matter (NOM) and turbidity from surface waters. In the present study another of our aims was to investigate whether pretreatment with coagulation combined with post-oxidation (US/O₃) can also remove NOM, turbidity and coliform from the same water resources. NOM and turbidity removal were measured by UV absorbance at 254 nm (UV₂₅₄) and a turbidimeter, respectively. Aluminum sulfate (alum), ferric chloride (FC), and poly aluminum chloride (PACl) were tested as coagulants. The disinfection potential of the US/O₃ process was evaluated by measuring coliform counts. The effects of different input variables including ozone dose, power intensity, ultrasound frequency, reaction time, coagulant type, dose of coagulant and coagulant aid were examined on the process performance. Design of experiments (DoE) and surface response methodology (RSM) techniques were employed to optimize the operating parameters. Individual coagulation process with ferric chloride decreased NOM and turbidity up to 33% and 15%, however pre-coagulation with ferric chloride combined with US/O₃ decreased NOM and turbidity 75% and 32%, respectively. PACl was the best coagulant in the sole coagulation, but in pre-coagulation combined with US/O₃ process, FC exhibited the best performance. Treatment with US/O₃ following pre-coagulation decreased the amount of coagulant and coagulant aid needed for the treatment. Pre-coagulation followed by US/O₃ improves the NOM, turbidity and coliform removal, and so could be considered as a potential method for removing NOM, turbidity and coliform.

Key words | NOM, post-oxidation, pre-coagulation, turbidity, ultrasound/ozone

HIGHLIGHTS
- Pre-coagulation combined with ultrasound/ozone (US/O₃) improved NOM and turbidity removal.
- The optimal coagulant type and concentration in the individual coagulation process were different from and higher than in the combination treatment.
- Among the experimental parameters of the US/O₃ process, the intensity was the most effective one for turbidity and NOM removal.
- US/O₃ post-oxidation process is a potential disinfection technique.
Natural organic matter (NOM) is the major contributor to odor, taste, and color of waters (Matilainen & Sillanpää 2010), and has been known as a precursor to the formation of disinfection by-products (DBPs) (Sadrnourmohamadi & Gorczyca 2015). NOM is present in all types of surface and ground waters, and consists of a range of compounds, from largely aliphatic to highly aromatic, as well as heavily charged to uncharged materials with a wide range of molecular sizes and chemical compositions. The amount of NOM in water resources changes with the climate and the hydrological regime as well as depending on a number of other environmental factors. Thus, the NOM content of waters varies with the source, season and environment, including floods, rainfall, and droughts (Matilainen & Sillanpää 2010). Due to the potential adverse health effects of DBPs, such as trihalomethanes (THMs), the removal of NOM from water resources has been considered as an important issue in water treatment technology (Sadrnourmohamadi & Gorczyca 2015). NOM can also lead to the fouling of water network systems and increase the levels of heavy metal complexes. In addition, these compounds can act as carriers for toxic pollutants such as radionuclides and pesticides (Matilainen & Sillanpää 2010), and may improve biofilm growth in water distribution systems (Matilainen & Sillanpää 2010; Al-Juboori et al. 2016a). Thus, effective treatment techniques should be applied to remove these compounds from surface waters.

Over the years, the demand for safe and high-quality drinking water has considerably increased due to population growth and the development of different industries. In this regard, dam reservoirs are considered as the main water suppliers for domestic, drinking and irrigation purposes. However, dam waters have higher levels of NOM, while they are less turbid due to the long retention time (months or even years) (Sharma 2015).

There are different conventional technologies, such as coagulation, sedimentation and filtration, which have widely been used for the treatment of water supplies; however, several shortcomings restrict their use, especially in large-scale configuration (Al-Juboori et al. 2016a). Conventional coagulation methods have been shown to mainly remove particular pollutants, but micro-pollutants such as NOM could not be removed effectively by these techniques. According to the previous evidence, these methods could only remove the high molecular weight fraction of NOM, while having a minor effect on the hydrophilic substances (Sillanpää et al. 2018). Of note, the hydrophobic components, including humic acids, humin and fulvic acids, are responsible for the largest fraction of NOM (Matilainen & Sillanpää 2010), and if left untreated, these compounds can result in the generation of THMs and halo acetic acids (HAA), which pose irreversible adverse effects to human health (Tubić et al. 2015).

Moreover, due to the complexity and negative surface charge, the optimum conditions for the removal of NOM do not always align with the removal of other forms of contamination, including turbidity (Yan et al. 2008; Al-Juboori et al. 2016b). Hence, to achieve high NOM and turbidity removal, especially in low turbidity waters such as dam reservoirs, higher dosages of coagulants and polymeric coagulant aids should be applied to increase the performance of the coagulation/flocculation process. This can result in the production of large amounts of sludge and increase the treatment costs (Al-Juboori et al. 2016a, 2016b).
Based on the mentioned notes, the removal of NOM by the conventional coagulation methods faces serious challenges (Matilainen & Sillanpää 2010), therefore enhanced treatment methods are needed for the effective removal of these compounds and turbidity from dam waters. During the past decades, the use of advanced oxidation processes (AOPs) along with conventional treatment technologies has largely been investigated. A large body of evidence indicates that AOP-based treatment methods could potentially attain better NOM and turbidity removal (Matilainen & Sillanpää 2010). Accordingly, it has been shown that the addition of chemical oxidation to the coagulation process can improve the removal of NOM (Al-Juboori et al. 2016b; Sillanpää et al. 2018). In such integrated systems, AOPs could oxidize and transform the higher molecular weight NOMs to lower molecular weight products, enhancing the removal efficiency (Matilainen & Sillanpää 2010).

Ultrasound irradiation (US) is another method that has been shown to increase the performance efficiency when combined with conventional methods and has some advantages including ease of installation, being environmentally friendly, and having low maintenance costs (Naddeo et al. 2007; Pham et al. 2009). The US irradiation system could degrade organic compounds mainly through the generation of short-lived oxidants, such as hydroxyl radicals (Al-Juboori et al. 2016a), and leads to reduced membrane fouling (Aiasghari Aghdam et al. 2013). It has been shown that a combined US and ozone (US/O₃) process has a synergistic effect on the oxidation of organic matter and could significantly remove these substances from the aquatic environment (Dietrich et al. 2017). US irradiation has also been reported to present a positive effect on the performance of the coagulation process (Al-Juboori et al. 2016b).

Previously we demonstrated that the treatment with US/O₃ followed by coagulation with PACL has a remarkable effect on the removal of NOM and turbidity from surface waters (Setareh et al. 2020). However, there are several studies suggesting that application of coagulation prior to the oxidation method removes high molar mass (HMM) NOM (Matilainen & Sillanpää 2010), and turbidity more effectively (Rahman et al. 2010). Therefore, in the present study we aimed to investigate whether pre-coagulation combined with post-oxidation (US/O₃) could remove NOM and turbidity compared with pre-US/O₃ followed by coagulation.

**MATERIALS AND METHODS**

**Source water characterization**

The water samples used in this study were collected from the Gavshan dam, in Kurdistan province, Iran. The samples were obtained from dam outlet water being fed to the water treatment plant, and were collected in 2 L pre-cleaned containers and transferred to the laboratory. The sampling, storage and measurements were done according to the 22nd edition of *Standard Methods for the Examination of Water and Wastewater* (APHA 2012). The general characteristics of the raw water samples, including turbidity, hardness, coliform counts, pH, alkalinity, turbidity, color and NOM, were analyzed and are summarized in Table 1. Turbidity was measured according to Standard Nephelometric Method 2130B, using a 2100P Portable Turbidimeter (Hach, USA). Color of raw water was determined according to Standard Visual Comparison Method 2120 B. The alkalinity and pH of the samples were determined in accordance with Standard Method 2520B and Standard Method 4500-HB, respectively using a pH meter (Hanna-H1 8519 N, Italy). Total and *Escherichia coli* counts were determined with culture in coliform agar media. The NOM was measured, according to Standard Method 5910B by using a spectrophotometer (UV-VISIBLE/XENON/HALOGENUV I Line 9300-9600, USA) with a quartz cell of 1 cm. Electric conductivity was determined in accordance with Standard Laboratory Method 2510 B, using a conductivity meter (WTW LF 196, Germany).

**Chemicals**

The chemicals used in this study were alum [Al₂(SO₄)₃·18H₂O], ferric chloride [FeCl₃·6H₂O], poly aluminum chloride (PACL, [Al₂(OH)₃·Cl₆e·YH₂O] Z), H₂SO₄ (0.02N), phosphoric acid, potassium indigo trisulfonate, Formazin (Merck, Darmstadt, Germany), sodium dihydrogen phosphate (Sigma Company), and coagulant aids. Two types of coagulants were used; one, Bes flocc (Korea), consists of anionic polyelectrolyte: K410AF, E300, and cationic polyelectrolyte K353CF; and the other, Magnafloc polyelectrolyte (BASF Company, Germany), consists of cationic polyelectrolyte (LT₃₀) and anionic polyelectrolyte (LT₂₅ and LT₂₇). All the chemical solutions...
and stocks used in this study were prepared by dissolving in distilled deionized water (DDW).

**Experimental setup**

The US/O₃ reactor used in the experiments is illustrated in Figure 1.

The reactor comprises an ultrasonic generator (Elmasonic, P 60 H, Germany) producing ultrasonic waves at oscillating frequencies of 24 kHz, 37 kHz and 80 kHz, and intensities of 100, 150 and 200 W/cm². The power intensity was adjusted based on the manufacturer’s instructions. Accordingly, the beam area was constant and power could be changed by pressing the power key. The maximum volume of the ultrasound tank was 5.75 litres with 5.1 kg weight.

Ozone was generated using a laboratory ozone generator (Ozo+ ARDA, model 10/GH, France) with 60 × 40 × 32 cm dimensions, equipped with air pump (ACO-5505-6.5W, China) and gaseous flow meter for measuring the discharge flow rate. The ozone generator was characterized by nominal airflow 5L/min and nominal ozone output 5 g/h, and work pressure of 0.3–0.7 bar. The gaseous ozone flow into the reactor was controlled at 1, 2, 3 ppm. The ozone dosage was adjusted by changing the flow of air entering the reactor by a flow gas meter. Ozone generation output and ozone concentration in the reactor were determined by the indigo method (Standard Method 4500-O₃ A, 22nd edition). The process sequence of US/O₃ with the coagulation process is shown in Figure 2.

### Table 1 | General raw water quality characteristics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristic</th>
<th>Parameter</th>
<th>Amount and standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gavshan dam water</td>
<td>Physicochemical parameter</td>
<td>pH</td>
<td>7.78 ± 0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alkalinity (mg/L_CaCO₃)</td>
<td>170 ± 4.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Turbidity (NTU)</td>
<td>1.65 ± 0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electric conductivity (μSiemens/cm)</td>
<td>380 ± 6.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Color (Pt-Co Hazen)</td>
<td>5 ± 0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hardness</td>
<td>182 ± 3.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UV_254 (cm⁻¹)</td>
<td>0.019 ± 0.0024</td>
</tr>
<tr>
<td></td>
<td>Bacteriological parameter total coliform (MPN/100 mL)</td>
<td>Total coliform (MPN/100 mL)</td>
<td>386 ± 500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Escherichia coli (No/100 mL)</td>
<td>25 ± 14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chlorophyceae (No/1,000 mL)</td>
<td>1,181 ± 1,239</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cyanophyceae (No/1,000 mL)</td>
<td>18 ± 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diatom (No/1,000 mL)</td>
<td>27,364 ± 27,469</td>
</tr>
<tr>
<td>Biological parameter</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Experimental design**

The response surface methodology (RSM) is an effective statistical tool for optimizing multiple variables. The software of DOE (version 7.0.0) was used for experimental design and data analysis in both individual coagulation and pre-coagulation combined with post-US/O₃. NOM and turbidity were chosen as two independent factors in the design. The ranges of the coded and actual unit variables are shown in Table 2. RSM based on three levels was used to obtain the best possible US/O₃ combination. The experiments were set according to NOM and turbidity removal. The experimental runs were created based on D-optimal design with seven factors. Independent variables were coded at three different levels (−1, 0 and +1) in the ranges defined by the preliminary experiments.

**Experimental procedure**

### Ozone generator calibration

The measurement of input and output ozone levels was done by using a colorimetric method with potassium indigo trisulfonate solution (in accordance with *Standard Methods*, 22nd edition (APHA 2012, Method 4500-O₃ A) and portable ozone meter.

### Jar test, coagulation

In the first step, we examined the effect of the coagulation–flocculation process on NOM and turbidity removal.
Accordingly, the influence of three variables including coagulant concentration, coagulant aid concentration, and coagulant type were examined on the process performance. In brief, the coagulation–flocculation test (ASTM 2005) was performed at room temperature using Phipps & Bird’s conventional six-paddle method (Richmond, USA). The coagulants were alum [Al\(_2\)(SO\(_4\))\(_3\)-18H\(_2\)O], ferric chloride (FeCl\(_3\)-6H\(_2\)O), poly aluminum chloride PACl [Al\(_2\)(OH)\(_3\)-Cl\(_3\)-YH\(_2\)O], used at dosages ranging from 0.5 mg/L to 1.5 mg/L. The coagulant solutions were prepared daily by mixing a concentration of 10 g/L of chemicals with distilled water (0.1 ml of test solution is equivalent to 10 mg/L while added to 1 L of the sample). The coagulant-aid powders were dissolved to obtain 0.1% stock solutions, which were then diluted to prepare working solutions with desired concentrations. As mentioned earlier, two types of coagulant aid, anionic and cationic polyelectrolyte (Bes floc, Korea) including K410AF and E500 and another (BASF, Germany),

![Schematic diagram of US/O\(_3\) set-up.](image)
including LT22, LT25, LT27 and K535CF, were used in this study. Based on our previous experiences, the dosages of polyelectrolyte varied from 0.1 up to 0.3 ppm. The coagulation process was performed with an initial rapid mix for 1 min at 120 rpm which was followed by a slow mix for 15 min at 30 rpm. Afterwards, the flocculated clays were allowed to settle and the effect of the coagulation on NOM removal was determined by absorption at 254 nm (UV254).

Optimization of US/O3 for turbidity and NOM removal

To determine the optimum US/O3 working conditions for turbidity and NOM removal, the effect of different parameters related to ultrasound irradiation and ozonation were examined separately. Accordingly, in order to optimize the ultrasound irradiation, we examined the effect of power intensities of 100, 150, 200 W/cm², sonication frequencies of 24, 37 and 80 kHz, and exposure times of 3, 5, 10 min. The reaction times throughout this study were defined based on ozonation time, thus the ozonation and sonication reaction times are the same (maximum 10 min). The efficiency of the process (ultrasound irradiation) was analyzed on the basis of changes before and after the process by measurements of UV254 and turbidity. In the next step, the effects of the various ozonation parameters including ozone dosage, contact time, ozone concentration, and hydraulic retention time on the rate of NOM and turbidity removal were studied. Hence, the ozonation was performed on raw water with different ozone dosages of 1, 2, 3 ppm, and time intervals of 3, 5, 10 min. The process efficiency was evaluated on the basis of changes before and after the treatment by measuring UV254 and turbidity. Subsequently, the effect of US/O3 on NOM (UV254) and turbidity removal was tested and the obtained results were compared with the results from untreated raw water samples. Ultimately, the effects of pre-coagulation combined with US/O3 post-treatment on turbidity and NOM removal were evaluated by measuring UV254 and turbidity, before and after the process under the same conditions.

RESULTS AND DISCUSSION

Source water characteristics

The general properties of the water samples obtained from Gavshan dam are summarized in Table 1. We observed higher amounts of biological materials in the studied samples compared with the previously reported dam water samples in the region. The pH of the samples was about 7
and the UV$_{254}$ absorbance was 0.019–0.025 cm$^{-1}$. As expected, due to the long retention behind the dam, the water samples were of low turbidity but had higher amounts of TOC. Based on the alkalinity analysis, the samples were moderately alkaline. Previous studies have shown that low temperature and low turbidity make it harder to achieve efficient treatment (Zhang et al. 2018). The NOM content of the water might also be dependent on the geology and surrounding anthropometric activities (Matilainen & Sillanpää 2010).

**NOM characterization of water samples**

In this study, fine organic matter (mainly including external organic matter, fragments of algal, periphyton and inorganic frustules of the diatoms) was the dominant pollutant of the water samples, which were assumed to be not completely removed by the use of coagulants and coagulant aids only (Setareh et al. 2020).

**NOM compounds of raw water samples**

Since the various components of the NOM could react differently during the treatment process, we performed NOM fractionation. To this end, organic components of the raw water samples were identified by GC/MS. Based on the GC/MS results (Figure 3), aromatic compounds such as toluene, and straight-chain alkane-based compounds including hexadecane, eicosane, octadecane, octacosane, docosane, and tetracosane were the main constituents of NOM isolated from the tested water samples. Furthermore, the octacosane (a non-polar hydrophobic alkane with chemical formula C$_{28}$H$_{58}$) was identified as the main fraction of NOM according to the area under the curve of the peaks. The results revealed that the hydrophobic fraction was responsible for the main part of TOC (Table 3). Similarly, Sadournmohamadi & Gorczyca (2015) have also demonstrated that over 70% of fractionated TOC was comprised of hydrophobic materials, where hydrophobic acid (humic substances) contributed to 50% of organic carbon fractions.

We assumed that toluene may be produced through the anaerobic hypolimnion. However, algae and lignin might be the origin of other fractions. In a previous study, Luning Prak et al. (2015) demonstrated that algae contribute most of the low molecular weight components in dam water samples, as well as some high molecular weight molecules, comprising n-hexadecane, n-octadecane, n-pentadecane, and n-heptadecane.

**Effects of individual coagulation process on NOM and turbidity removal**

As mentioned earlier, the effect of three different coagulants (alum, ferric chloride, and PACl), two types of coagulant aids (ionic and cationic polyelectrolytes) and different coagulant dosages were examined on process performance and the resultant data were used to choose the optimal conditions. Based on the obtained results, a favorable reduction of turbidity (18%) and NOM content

![Figure 3](image_url)

**Table 3**: Components identified in raw water

<table>
<thead>
<tr>
<th>Raw Compounds</th>
<th>MW</th>
<th>Retention time (min)</th>
<th>Peak area</th>
<th>Hydrophilic</th>
<th>Hydrophobic</th>
<th>Source of compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Toluene</td>
<td>92.063</td>
<td>2.969</td>
<td>2,157,671</td>
<td></td>
<td>o</td>
<td>Hypolimnion layer, lignin</td>
</tr>
<tr>
<td>2 Octadecane</td>
<td>254.297</td>
<td>20.2</td>
<td>2,476,884</td>
<td></td>
<td>o</td>
<td>Algal HRD</td>
</tr>
<tr>
<td>3 Hexadecane</td>
<td>226.266</td>
<td>17.445</td>
<td>2,312,787</td>
<td></td>
<td>o</td>
<td>Algal HRD</td>
</tr>
<tr>
<td>4 Tetracosane</td>
<td>338.391</td>
<td>27.101</td>
<td>2,639,862</td>
<td></td>
<td>o</td>
<td>Red alga</td>
</tr>
<tr>
<td>5 Docosane</td>
<td>310.36</td>
<td>24.995</td>
<td>2,384,387</td>
<td></td>
<td>o</td>
<td>Red alga <em>Jania rubens</em></td>
</tr>
<tr>
<td>6 Eicosane</td>
<td>282.329</td>
<td>22.701</td>
<td>2,447,836</td>
<td></td>
<td>o</td>
<td>Red alga <em>Jania rubens</em></td>
</tr>
</tbody>
</table>
(60%) was attained at working conditions of 0.81 ppm PACI, 0.1 ppm anionic polyelectrolyte BASF LT25 (Table 4).

The ANOVA analysis of turbidity removal efficiency in the coagulation process alone with the quadratic model is shown in Table 5. The value of $R^2$ was 0.8517 in this analysis. Coagulant concentration ($A$), coagulant ($C$), $A^2$, $AC$ were significant terms for the model. Other $P$-value modeling terms were not statistically significant ($P$-value $\geq 0.05$).

In agreement with our findings, several studies have shown that PACI is one of the powerful coagulates in reducing turbidity (Yan et al. 2008; Pirsaheb et al. 2016). Furthermore, similar to the present study, it has been shown that by the increase of coagulant dosage, process efficiency is increased (Pirsaheb et al. 2016). There is also evidence showing that PACI can remove fractional DOC (D-NOM or DOC) more effectively than the other coagulants. Additionally, PACI could increase the rate of particle destabilization, increasing the treatment efficiency (Yan et al. 2008). However, the effectiveness of treatment by coagulation could be affected by different parameters including the type and dosage of the coagulant, solution pH and temperature, NOM characteristics, and the presence of bicarbonate, chloride, and sulfate anions in the water environment (Sillanpää et al. 2018). Several studies have shown that NOM is the most important parameter, should be considered in the design of treatment processes and determines the amount of coagulant needed (Matilainen & Sillanpää 2010; Al-Juboori et al. 2016a). It has been revealed that coagulation methods only remove the high molecular weight fraction of NOM (1,000–4,000 g/mole), while having a minor effect on the hydrophilic compounds (Yan et al. 2008; Sillanpää et al. 2018). This can be explained by evidence showing that the removal of high molar weight NOM mainly occurs by charge neutralization, whereas adsorption on surfaces of metal hydroxides is the mechanism that underlies the removal of low molecular weight NOM using the coagulation process (Yan et al. 2008). Therefore, an individual coagulation process is not effective for the removal of NOM and higher amounts of coagulants/coagulant aids are needed to remove NOM to a desirable level (Sillanpää et al. 2018).

The accuracy of the model in predicting the experimental results was also illustrated by predicted vs actual (Figure 4). It is obvious that the estimated data were close to the actual results.

Interaction between the coagulant type and the polymer aid at different concentrations in turbidity removal for individual coagulation is shown in Figure 5. Due to the interaction between alum and ferric chloride coagulants, the performance of alum and ferric chloride was similar for the removal of turbidity. Meanwhile, by increasing the concentration of coagulants, the effect of ozone on turbidity removal was increased. Furthermore, a low amount of coagulants is needed by the increase of ultrasound intensity.

### Effects of pre-coagulation combined with US/O3 (post-oxidation) on NOM, turbidity and coliform removal

We examined the effects of US/O3 on the removal of NOM and turbidity in coagulated samples. The optimum working conditions for the US/O3 process were obtained at 3 mg/L ozone coupled with sonication at higher frequency.

#### Table 4 | Effect of coagulation alone on turbidity and NOM removal of raw water in the condition of optimum coagulants and coagulant aid use

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Coagulant types</th>
<th>Coagulant dose (ppm)</th>
<th>Coagulant aid dose (ppm)</th>
<th>NOM removal (%)</th>
<th>Turbidity removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PACI</td>
<td>0.81</td>
<td>0.1</td>
<td>60</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>Alum</td>
<td>1.01</td>
<td>0.1</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>Ferric chloride</td>
<td>0.94</td>
<td>0.1</td>
<td>33</td>
<td>15</td>
</tr>
</tbody>
</table>

#### Table 5 | ANOVA results for design expert on turbidity response

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Probability</th>
<th>$R^2$</th>
<th>$Adj.R^2$</th>
<th>Adeq. precision</th>
<th>SD</th>
<th>CV</th>
<th>PRESS</th>
<th>Probability for lack of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>&lt;0.0001</td>
<td>0.8517</td>
<td>0.8214</td>
<td>23.966</td>
<td>3.18</td>
<td>3.66</td>
<td>1,169.06</td>
<td>0.4050</td>
</tr>
</tbody>
</table>
(80 kHz) and intensity of 200 W/cm². As shown in Figure 6, the process performance increased by the increase of US frequency. This might be due to ultrasonic irradiation at higher power producing strong cavitation resulting in wave shock and generation of reactive free radicals (e.g., ·OH and H₂O₂) via the violent collapse of cavitation bubbles, thus improving the process performance (Naddeo et al. 2010).

It has also been shown that at higher wave frequencies the quantity of collapsing bubbles is higher than at lower wave frequencies (Al-Juboori et al. 2016c).

In addition, the increase of US power intensity has also increased the process efficiency. These results are in agreement with the findings of Stepniak et al. (2012), who reported that higher power intensity could increase the efficiency of the combined US/O₃ process in removing NOM and turbidity, mainly by reducing the hydrophobic fractions.
According to the results, under the optimal US intensity and frequency (200 W/cm², 80 kHz) the NOM and turbidity removal was increased by increasing reaction time and ozone dosage (Figure 7).

These findings indicate that the addition of ozone to the US process could enhance radical generation (Stępnia et al. 2012), and enhance the efficiency of process performance (Lesko et al. 2006; Al-Hashimi et al. 2012; Dietrich et al. 2012).

Ozone particularly attacks the double bonds of humic acids as the main fractions of NOM (Haarhoff et al. 2010). Other studies have also shown that ozone molecules can quickly react with carbon-carbon double bonds and with the fractions of NOM having high electron density. These reactions can break high molecular weight NOM moieties to low molecular weight intermediates, and thus result in turbidity removal and decreased UV absorbance (Hua & Reckhow 2006). On the other hand, ultrasound application results in inactivation of algal cells and effective removal of algal turbidity, thus improving the removal of low turbidity water (Fast et al. 2014). Based on the results, the application of US/O₃ following the coagulation process (pre-coagulation, post-oxidation) increased the NOM and turbidity removal by 42% and 17%, respectively compared with individual coagulation. The decrease in UV₂₅₄ absorbance following the application of US/O₃ confirms the possible changes in the aromatic structure of the humic acid component of NOM as well as the transforming of high molar mass to low molar mass NOM moieties along with decreased DOC concentration. These findings clearly demonstrate the synergistic effect of US/O₃ on process performance (Lesko et al. 2006; Stępnia et al. 2012). Another study has also shown that the combined AOP–coagulation process could increase the treatment efficiency (Samadi et al. 2012). It has been shown that the combination of coagulation with AOPs could further increase NOM removal (decrease of UV₂₅₄ absorbance) (Özdemir & Güngör 2017). In ozone-based AOPs, ozone could favorably react with humic substances, mostly by electrophilic substitution and oxidation reactions, hence resulting in significant removal of UVA₂₅₄ and reducing the levels of DBP (Haarhoff et al. 2010). Therefore, the addition of ozonation could favor the achieving of higher NOM removal.

In line with previous studies, it is expected that pre-coagulation removed the particulate part of NOM. However, the remaining part of NOM, mainly non-humic substances (Bose & Reckhow 2005), was removed by the further US/O₃ process. There is evidence indicating that ozone has positive effects on non-humic organic matter. Furthermore, at higher concentrations (2.5 and 3.0 mgO₃/L), ozone could also react with hydrophilic compounds and thus mineralize higher amounts of NOM (Song et al. 2014). Accordingly, it can be concluded that the addition of the US/O₃ process to pre-coagulation can remove the remaining hydrophobic fraction and non-humic fraction of NOM which was not removed by coagulation.

Our results demonstrated PACI to be the best coagulant to remove NOM and turbidity when used in the sole coagulation process (Pirsaheb et al. 2016; Setareh et al. 2020). Interestingly and in contrast, FeCl₃ was the most effective coagulant when pre-coagulation was combined with the US/O₃ process. In other words, the highest removal of NOM and turbidity was achieved by pre-coagulation with FeCl₃ followed by US/O₃ (Figure 8). These findings indicate that the application of AOP combined with coagulation,
along with affecting operational parameters such as optimum coagulant dose, can also affect the type of coagulant used. Compared with the individual coagulation process, in the pre-coagulation, post-US/O3 process, lower coagulant (0.98 ppm) and anionic polyelectrolyte BASF LT25 (0.2 ppm) concentrations were used to remove NOM and turbidity to a desirable level. Our findings are in accordance with those previous studies that have shown that ferric salts could remove NOM (Sillanpää et al. 2018), and a larger proportion of DOC fractions (Umar et al. 2016), in comparison with aluminum salts. Moreover, ferric chloride has been demonstrated to be more efficient removing NOM with high molecular mass (up 3,000 g/mol) than alum. This is probably due to the high cationic charge of ferric chloride in contrast to alum, which results in more floc formation. Furthermore, due to the health issues, recent data support the use of ferric coagulants over aluminum counterparts (Sillanpää et al. 2018).

We observed higher NOM and turbidity removal with increase of the reaction time; however, the highest removal was obtained at 7 min reaction time (Figure 9). Similar results have also been reported by previous studies, indicating the increase of reaction time could enhance process performance (Al-Juboori et al. 2016c). We also observed that the application of US/O3 following coagulation could entirely remove coliforms from raw water. Therefore, this process has the potential to be used as a disinfecting method in water treatment. Results of the other studies have also demonstrated that treatment with ozone alone led to a substantial reduction while ultrasound alone exhibited only a small reduction. This could be explained by the synergetic effect of combined ultrasound and ozone treatment on the biological disinfection of water (Al-Hashimi et al. 2015). Similar results have also been reported by previous studies (Cho et al. 2005; Zhao et al. 2015). These findings can be explained by two physicochemical mechanisms: (1) by decomposing ozone molecules, ultrasound augments the generation of free radicals; (2) integrated ultrasonic treatment could enhance the aeration constant, (KLa-value). Both mechanisms contribute to the higher production of free radicals, which increases the process efficiency. All large bodies of evidence have shown free radicals to be strong disinfectant and oxidative agents in both ozonation and sonozonation processes (Dahl 1976).

In our previous study, we showed PACL to be the most effective coagulant in the sole coagulation and in the US/O3 pre-treatment-coagulation process to remove NOM and turbidity from surface water (Setareh et al. 2020). But, as demonstrated in this study, in the pre-coagulation followed by US/O3 process, PACL was less effective than FeCl₃. Furthermore, by comparing the results of the present research (NOM and turbidity removal of 75% and 32%, respectively) with those of our previous findings (NOM and turbidity removal of 95% and 50%, respectively), it is obvious that the pre-US/O3-coagulation process has superiority over the pre-coagulation–post US/O3 process in removing NOM and turbidity from surface waters; however the differences were slight and not marked.

CONCLUSION

The combination of US/O3 post-oxidation with coagulation enhanced NOM and turbidity removal.
1. Pre-coagulation with ferric chloride has superiority over PACI or alum in NOM and turbidity removal when combined with post-US/O₃.
2. The optimal coagulant type and concentration in the individual coagulation process were different from those observed for the combination pre-coagulation–post US/O₃ process.
3. The post-coagulation (pretreatment with US/O₃ followed by coagulation) had better activity in removing NOM and turbidity compared with pre-coagulation (pretreatment with coagulation followed by US/O₃).

According to the results of the present study, the US/O₃ process has the potential to be combined with coagulation (either before or after the coagulation) to remove NOM and turbidity from raw waters. The addition of US/O₃ to coagulation has economic effects as it can increase process performance, while reducing the amount of coagulants used and with less sludge produced by using this combined system.

ACKNOWLEDGEMENTS

This work was supported by the deputy of Research and Technology of Kermanshah University of Medical Sciences (Grant number 96191).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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Matilainen, A. & Sillanpää, M. 2010 Removal of natural organic matter from drinking water by advanced oxidation


First received 17 August 2020; accepted in revised form 2 November 2020. Available online 16 November 2020