

Effects of Ferrate (VI) pre-oxidation in the coagulation treatment of drinking water

ABSTRACT

Although ferrate (Fe(VI)) is introduced as a feasible replacement for pre-oxidation in the treatment of drinking water, limited research is available on effects of utilizing ferrate for the treatment of drinking water sources to produce potable water. In the present study, an experimental program was conducted on the employment of ferrate in drinking water treatment; this program included batch and continuous flow tests on multiple samples of natural water from different sources. According to the batch test results, the ferrate pre-oxidation led to improved ultraviolet light-absorbing compounds (UV254) removal by subsequent coagulation in a small portion of the samples but showed no enhancement in the majority of samples. In continuous flow tests, ferrate was added to small-scale models of existing treatment plants. Compared to the case with no pre-oxidation, ferrate pre-oxidation generally enhanced UV254 absorption, finished water turbidity, and disinfection by-product formation. Therefore, ferrate can be viably used in the treatment systems of drinking water and provide a superior replacement to available oxidants by allowing for the oxidation and disinfection of inorganic materials without negative effects on downstream processes. More researches are needed to examine a more viable combination of ferrate with other methods and obtain more knowledge about the mechanisms of the known synergistic applications of ferrate.

Keywords: Water treatment, Pre-oxidation, Ferrate, UV254

1. INTRODUCTION

Humanity is facing the verge of a global water crisis due to the rising extraction of water from water resources that are already under stress by pollution, exploitation, and climate change [1]. Due to the current phase of worldwide economic stagnation, resources available to expand water treatment are limited. A combination of the mentioned factors has placed considerable stress on water systems [2-3]. This combination of factors necessitates technological innovations to reinforce water systems and create greater capacity, adaptability, and energy efficiency [4]. To accomplish these goals, it is necessary to produce greater volumes of higher-quality water from supplies that are experiencing potential degradation while lowering energy consumption [5].

Ferrate (Fe(VI)) is touted as an emergent “green chemical” for the treatment of drinking water [6]. Ferrate presents the main benefit of high oxidation capacity without producing halogenated by-products [7]. Moreover, the oxidation byproduct of ferrate, ferric iron (Fe(III)), may present positive effects on downstream particle destabilization and removal processes [8]. Furthermore, due to its disinfectant features, ferrate may also be able to inactivate pathogens in drinking water [9]. The mentioned multi-faceted action modes of ferrate yield potential efficiency that is valuable for water treatment facilities [10]. Due to this feature of ferrate, it is also an interesting choice for smaller facilities with limited resources, for which

adapting to rising water system stresses may be especially challenging [11]. Since obstacles such as the need for considerable financial investment or significant changes to available mechanical systems do not limit the use of ferrate, it can improve environmental equality via allowing for a fair distribution of environmental benefits [12].

Therefore, many researchers have recently become interested in using ferrate as a highly-efficient pretreatment to **implement** a new strategy for water treatment.

For example, researchers performed the bench-scale tests to investigate ferrate treatment as an essential substitute process for traditional water treatment. Results showed that ferrate could effectively remove turbidity in a single dose and the treatment efficiency was strongly dependent on ferrate dose and pH [13]. In other study, ferrate was used for surface water treatment to improve ultra-filtration efficiency. All of the fluorescent components were effectively removed to different levels. Using $\text{Fe(VI)}=0.05$ mM decreased the dissolved organic carbon by 44.33% [14]. Also, the study conducted to validate the practical feasibility of ferrate used as an alternative to the existing coagulant for water treatment. A ferrate dose of 0.1 mg/L can achieve 93% particle removal (in terms of particle counting) after the filtration [15].

However, despite the advantages of ferrate application, limited research is available on the effects of employing ferrate to treat drinking water. Moreover, limited research has addressed the effects of using ferrate on the treatment of drinking water such that multiple probable outcomes are taken into account. Although several studies have investigated the use of ferrate in the oxidation of different specific compounds, a majority of them have been laboratory studies that used phosphate buffers and incorporated other simplifying conditions that are rarely practical for the treatment of drinking water.

Hence, this study was mainly aimed at evaluating the effects of ferrate application in the treatment systems of drinking water. To that end, ferrate was added to pilot-scale and bench-scale treatment systems to mimic the full-scale treatment process of many operational facilities. Tests using these systems examined the impact of ferrate incorporation on important parameters in water treatment including turbidity, disinfection by-product formation potential (DBPFP), and organic compounds concentration.

2. MATERIAL AND METHODS

2.1. Batch experiments

As a buffer for the raw water obtained from several sources, 10 mM borate was used, and ferrate was directly incorporated as a pre-oxidant as a K_2FeO_4 salt at a fast-mixing rate at ambient temperature (21 °C). An indirect indicator spectrophotometric method was employed to measure ferrate concentrations [16]. Two ferrate doses were used: 25 μM and 50 μM , selected according to the literature [17-18]. To cover the range of pH normally seen in the treatment of drinking water, two pH levels of 6.2 and 7.5 were selected to conduct Fe(VI) pre-oxidation. After a minimum reaction time of 45 min, a fraction of the obtained solution was analyzed for different parameters, while the rest of the solution was subjected to coagulation.

A common jar test procedure was used. Coagulation was executed based on [19]. The jar test was conducted by a programmable flocculator (Kemwater, Kemira). Several doses of ferric chloride were added to the samples at fast mixing rate ($G\sim 200$ sec^{-1}), followed slow mixing for 10 min ($G\sim 50$ sec^{-1}). To maintain the pH at 5.5, 1 M NaOH or 1 M HCl was added in a dropwise manner, as necessary. After flocculation, the solution was settled in quiescent conditions for 30 min. Next, after removing a 20mL sample from the reactor, it was filtered

with a fine glass fiber filter (Whatman GF/F) with an effective size exclusion of 0.7 μm . After measuring the UV 254 absorbance of jar test samples, the Fe(III) dose yielding the minimum UV 254 absorbance value was considered as the optimum ferric dose (OFD). In case of obtaining the same UV 254 absorbance per different doses ferric coagulant (for example, <5% difference), the smaller of the two doses was considered as the OFD. Since UV 254 absorbance is a very suitable surrogate parameter to estimate organic carbon (OC) concentrations in natural water, it was selected as the main parameter for measurement [20-21]

2.2. Water samples

To obtain water samples utilized in the batch tests, 11 separate surface water sources in Mazandaran province, Iran, were used. The collected water samples were general representatives of surface water sources in northern Iran: low turbidity, low hardness, with medium to high dissolved organic matter levels. All of the considered water sources lacked notable levels of inorganic contaminants including iron, arsenic, or manganese. Hence, the pre-oxidation was focused on removing organic materials and minimizing disinfection byproduct (DBP) formation potential. Table 1 gives information on the quality of the water samples under study.

Table 1. Details on the quality of water samples for the batch test

Sample No.	TOC (mg/L)	DOC (mg/L)	UV254 (1/cm)	SUVA (L/mg/m)	OFD (mg/L as Fe)	pH
1	3.3	3.1	0.09	2.9	6	7.1
2	5.9	5.2	0.22	4.1	12	6.6
3	6.4	5.8	0.11	1.8	10	7.0
4	2.9	2.7	0.08	2.0	4	6.6
5	1.7	1.5	0.06	4.0	5	6.5
6	3.3	3.2	0.14	4.3	10	7.2
7	4.4	4.3	0.16	3.7	11	6.5
8	2.8	2.8	0.11	3.8	11	6.5
9	2.0	2.0	0.04	2.1	4	6.5
10	2.0	2.0	0.12	6.0	4	6.0
11	2.1	2.1	0.08	3.6	6	7.0

Two water samples (sample 1 and sample 11) were considered in the batch tests for continuous flow experiments. Table 2 gives further details on the treatment parameters for these two samples.

Table 2. Continuous flow experimental parameters

Treatment parameter	Sample 1	Sample 11
Coagulant type	Cationic polymer (Nalco 8100)	Cationic polymer (Chemtrade EC-461)
Coagulant dose (mg/L as product)	6.9	5.9
Coagulant pH	6.9	7.5
Ferrate dose (μM)	25	50
Filter run time (h)	8	8

2.3. Continuous flow experiments

To construct the continuous flow system, a PVC pipe, certified for use with potable water by NSF 61, was used. A concentrated (1 mM) Fe(VI) solution was added before coagulation and clarification; this was followed by about 40 min of ferrate contact time through a series of two continuous flow stirred tank reactors. To prepare the stock solution of Fe(VI), K_2FeO_4 with purity of 97% (Battelle Corporation) was dissolved in deionized water. This pre-oxidation phase was followed by adding coagulants and pH control chemicals before an inline static mixer (as can be seen in detail in Table 2). This was followed by the flow of water to the up-flow adsorption clarifier (AC) and then down through a conventional anthracite (15 inches) over sand (9 inches) dual-media filter. The AC and media filter had hydraulic load rates of respectively 20 and 10 m/h. The monitoring of head loss was conducted across the dual media filter. Different instruments were used to measure turbidity and UV 254 values every minute after filtration with online flow. Per each water source, two tests were performed: one in the absence and the other in the presence of ferrate, with other factors were kept constant. Thus, the effect of incorporating ferrate into the treatment process train could be directly evaluated.

2.4. Analytical methods

A visible/ultraviolet light spectrophotometer with forward optics (Genesys 10S, Thermo Scientific) was used to measure UV 254 absorbance. Before measuring the absorbance of light with wavelength of 254 nm in 1 cm path length quartz cell, a GF/F filter was used to filter all samples for the measurement of UV 254 absorbance. To measure turbidity, a laboratory turbidimeter meeting the reported regulations of EPA Method 180.1 was used (2100N, HACH). In addition, alkalinity was determined in a colorimetric manner via titration [22]. Pressure transducers were employed to record head loss through the dual-media filter (Series 200, Noshok).

To quantify OC, a Shimadzu TOC-VCPH carbon analyzer was used to measure non-purgeable organic carbon. The instrument was calibrated using 10 mg/L of hydrogen phthalate as a standard. Before analysis, 6 N HCl and nitrogen were used to acidify and purge all the samples, respectively. The measurement of OC was compliant with standard methods section 5310B [22].

To initiate DBPFP measurement, buffered samples (pH=7.0, 10 mM phosphate) were chlorinated in 300 mL chlorine demand free, headspace free bottles and incubated for 72 hours at 20 °C. Chlorine doses were considered so as to obtain a residual of 3-5 mg/L as Cl_2 after the incubation phase. Following the incubation of the samples, they were analyzed for four trihalomethanes (THMs) and nine haloacetic acids (HAAs). To measure THMs, liquid/liquid extraction with pentane and then gas chromatography (GC) with electron capture detection (ECD) were conducted; this procedure was compliant to USEPA Method 551.1. The measurement of HAAs included the following: liquid/liquid extraction with methyl-tertiary-butyl-ether (MTBE), derivatization with acidic methanol, and analysis by GC-ECD. The analysis of HAAs was compliant to USEPA Method 552.2.

3. RESULTS AND DISCUSSION

3.1. Batch experiments

Fig. 1 presents the UV 254 absorbance results after coagulation at the OFD in the presence and absence of ferrate pre-oxidation at different doses and pH levels. In samples 3, 4, 10, and 11, compared with coagulation alone, ferrate pre-oxidation after coagulation resulted in smaller UV 254 absorbance. At pH of 6.2, this effect was greater in case of pre-oxidation than at 7.5. Nevertheless, in most of the samples, the removal of UV 254 absorbance was not significantly affected by coagulation with Fe(VI) pre-oxidation, in comparison with only coagulation with FeCl_3 . Ferrate pre-oxidation has a similar effect on DBP formation after chlorination [8]. After ferrate pre-oxidation, the samples generally did not show noticeable OFD changes, as can be seen in Table 3 for the samples 2, 4, and 5, while the OFD declined by 16%, 33% and 40%, respectively.

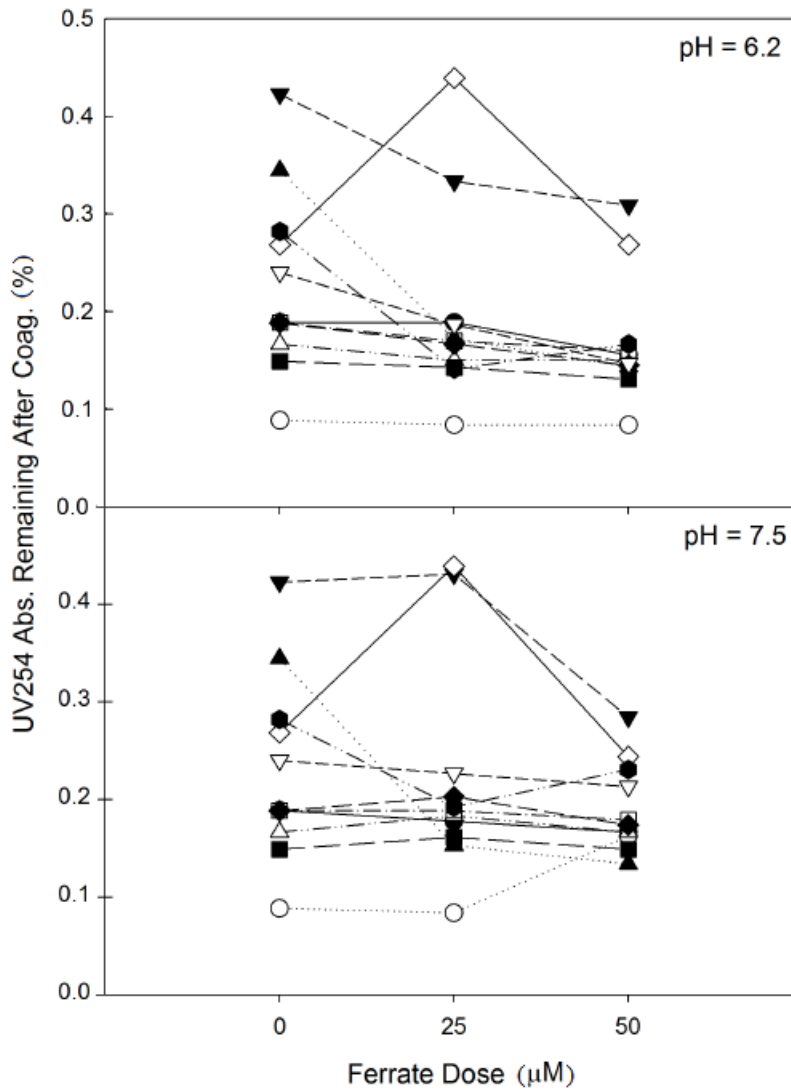


Fig. 1. UV 254 absorbance after coagulation at optimum dose of FeCl₃ in the presence and absence of ferrate pre-oxidation; coagulation pH=5.5 and borate buffer=1 mM

Table 3. Optimal doses of ferrate in the presence and absence of ferrate peroxidation

Utility	Optimal ferric dose (mg/L)				
	No ferrate	25 µM, pH=6.2	25 µM, pH=7.5	50 µM, pH=6.2	50 µM, pH=7.5
Sample 1	6	5	6	6	6

Sample 2	12	10	10	10	10
Sample 3	10	9	10	10	9
Sample 4	6	4	4	5	5
Sample 5	5	4	4	3	5
Sample 6	11	11	11	11	11
Sample 7	10	10	10	10	10
Sample 8	11	11	11	11	11
Sample 9	4	4	4	3	3
Sample 10	4	4	4	3	4
Sample 11	6	6	6	6	6

3.2. Continuous flow tests

To examine impact of pre-oxidation with ferrate on UV 254 absorbance by downstream processes, continuous flow tests were used. As can be seen in Fig. 2, dual media filter effluent UV 254 absorbance was recorded together with turbidity and filter head loss. For the two considered samples (samples 1 and 11), it is initially seen that the turbidity trends are declining, which can result from filter ripening. After establishing steady performance, the UV 254 absorbance of sample 1 in the presence and absence of Fe(VI) pre-oxidation was around 0.050 and 0.045 cm^{-1} , respectively. This indicates an around 10% decline in UV 254 absorbance due to pre-oxidation compared with the case without pre-oxidation. Similarly, for sample 11, the UV 254 absorbance in the presence of absence of Fe(VI) pre-oxidation was around 0.028 and 0.022 cm^{-1} , respectively, showing a decline of around 20% due to pre-oxidation.

In terms of turbidity, the test data of continuous flow exhibit a pattern similar to UV 254 absorbance, namely smaller turbidity values due to ferrate pre-oxidation. In the presence and absence of ferrate pre-oxidation, turbidities were 0.22 and 0.12 NTU for sample 1 and 0.09 and 0.08 NTU for sample 11, respectively. Sample 1 showed a more notable relative turbidity improvement.

There was no correlation between the further turbidity removal and UV 254 absorbance and an increased head loss across the dual media filter. Fig. 2 shows the results of the initial clean-bed head loss in inches of H₂O. For both samples, head loss progress through the dual media filters in the presence and absence of ferrate was generally negligible as a result of the previous clarification. Nevertheless, for the two samples with pre-oxidation, head loss experienced a relatively fast rise in the first hour of operation and a much slower increase as the operation continued. Finally, very similar head loss values were observed for the two samples and pre-oxidation conditions. Adding ferrate pre-oxidation led to no negative effect on capacity of the AC or dual media filter for successful operation in the filter run length of interest.

UNDER PEER REVIEW

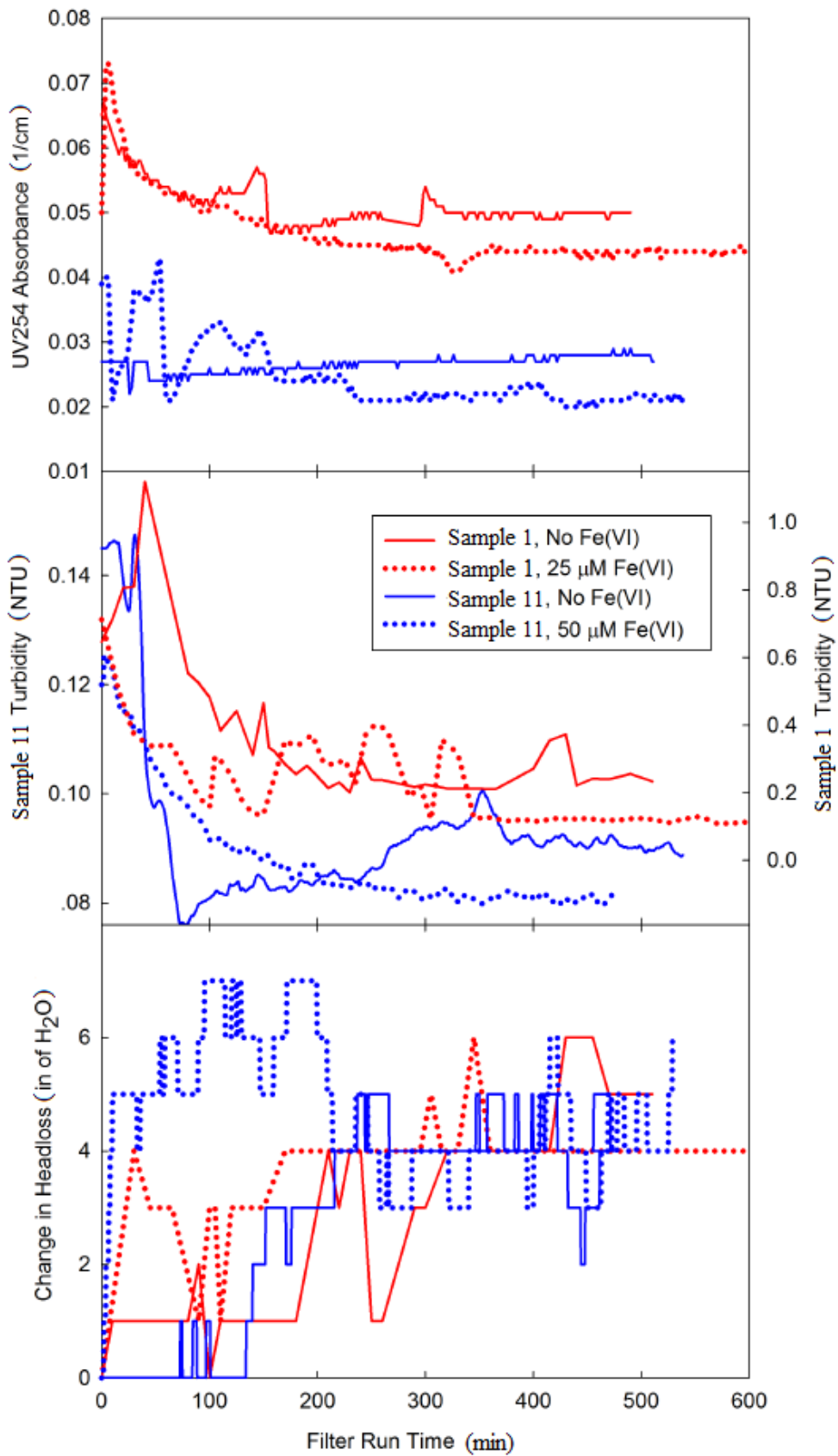


Fig. 2: UV254 absorbance, turbidity and head loss results from continuous flow experiments

Fig. 3 gives the DBPFP analysis results after filtration and chlorination for continuous flow tests. Trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) levels in the tests were higher in sample 1 than sample 11. These results are similar to those of UV 254 absorbance for the continuous flow tests, in which remaining UV 254 absorbance was higher in sample 1 than in sample 11. In sample 1, THMFP and HAAFP concentrations declined from around 105 to 90 $\mu\text{g/L}$ due to ferrate pre-oxidation. In addition, DBPFP experienced a smaller decline in sample 11, despite the fact that the Fe(VI) dose was twice that utilized for sample 1 (25 vs. 50 μM). Moreover, different effects of Fe(VI) on DBPFP across various water qualities were also observed in batch tests [23].

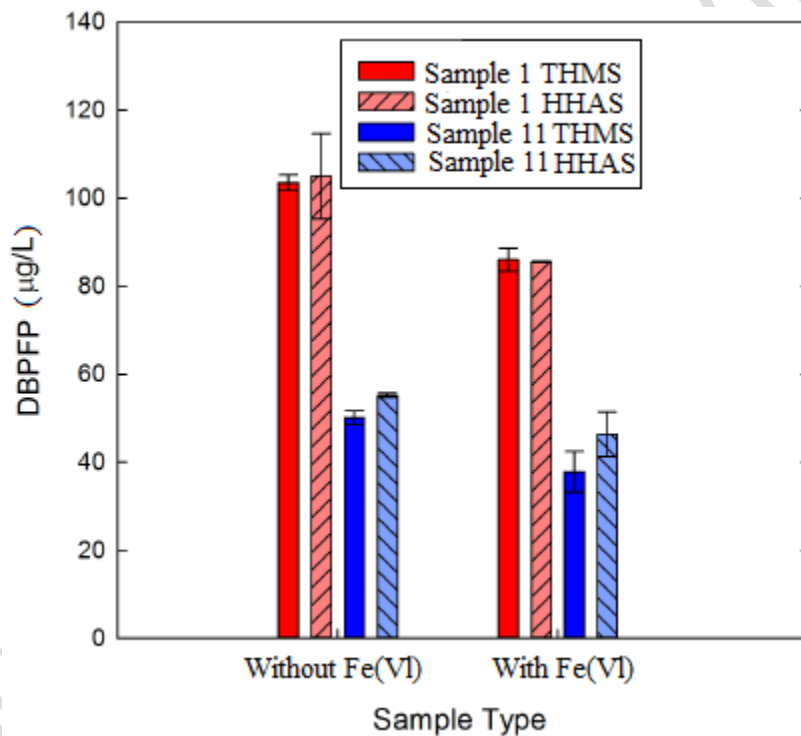


Fig. 3: Continuous flow DBPFP results for samples 1 and 11; for sample 1, Fe(VI)=25 μM and for sample 11, Fe(VI)=50 μM

According to the results of UV 254 absorbance for the batch tests, Fe(VI) pre-oxidation moderately affected the following coagulation to remove humic substances in comparison to coagulation with FeCl_3 with no pre-oxidation. In some case, Fe(VI) pre-oxidation enhanced UV 254 absorbance removal, while it failed to do so in most cases. In the majority of the water samples, ferrate pre-oxidation resulted in insignificant reductions in the OFD. This variable impact of Fe(VI) may result from the variable properties of natural organic matter, considering the fact the mixing conditions and pH were kept the same in all the batch tests. Previous studies have also reported the variable impact of ferrate on coagulation and

assigned this observation to oxidation impacts of ferrate on organic matter, which includes the cleavage of additional humic macro-molecular structures into more hydrophilic ones [24-25]. The cleavage of organic structures has also been reported after pre-oxidation with ozone [15,26].

In the batch tests, in case of the improvement of UV 254 absorbance removal by Fe(VI) following subsequent coagulation, pre-oxidation at pH 6.2 generally led to the greater benefit compared with oxidation at pH 7.5. Nevertheless, decay of ferrate in natural water strongly depends on pH, and decay rate decreases with increasing pH [27]. Thus, the trend of UV 254 absorbance removal was increasing even when ferrate exposure (namely dose and time) declined. This may be attributed to an increased Fe(VI) oxidation potential with decreasing pH [28]. On the other hand, findings indicate a more intricate association of Fe(VI) with reduction by-products (Fe(V) and Fe(IV)), whose formation from ferrate decay has been established [8,29]. Ferryl(IV) and perferryl(V) have the potential to react with many oxidants demands [11], and these two species have very short half-lives; this complicates spectrophotometric measurements [30]. Fe(V) and Fe(IV) may have key contributions to the removal of NOM via pre-oxidation and the following coagulation, which would not be dependent on pH and be more noticeable along with the decay of Fe(VI) into more reduced iron forms.

The two continuous flow tests on samples 1 and 11 demonstrated that ferrate pre-oxidation led to a general improvement in the quality of finished water relative to the case without pre-oxidation. According to the findings, Fe(VI) addition could improve the quality of finished water due to full-scale treatment simulation for both treatment systems. Fe(VI) pre-oxidation lowered the turbidity and UV 254 absorbance values of the filtered water, without affecting the filter run time. Fe(VI) pre-oxidation also decreased DBP formation potential.

4. CONCLUSION

In batch tests with many raw water samples, pre-oxidation by Fe(VI) had variable effects on UV 254 removal with the following coagulation. A number of cases showed enhanced UV 254 removal using Fe(VI) pre-oxidation. In most cases, effect was insignificant relative to coagulation with no pre-oxidation. In continuous flow test, Fe(VI) pre-oxidation enhanced UV 254 absorbance, turbidity, and DBP levels in finished water, relative to treatment with no pre-oxidation, without other detrimental water quality or operational impacts. Assessment of ferrate via continuous flow tests allowed for the evaluation of potential operational or engineering problems arising from incorporating ferrate pre-oxidation to an existing treatment system for drinking water. Ferrate incorporation had an insignificant effect on head loss in dual media filters after clarification by an up-flow adsorption clarifier. Head loss measurements across the AC were not made; however, during the experiment of samples 1 and 11, negligible head loss development was observed across the AC (for example, inches of H₂O following several operation hours).

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