

# IJCST 2017\_Effect of Permanganate Preoxidation to Natural Organic Matter and Disinfection by-Products Formation Potential Removal

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## Effect of Permanganate Preoxidation to Natural Organic Matter and Disinfection by-Products Formation Potential Removal

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**Abstract.** Laboratory scale experiments was conducted to examine effect of permanganate ( $\text{KMnO}_4$ ) peroxidation in characterizing and to remove natural organic matter (NOM) in source water. The experimental results shows that increasing permanganate dosage could decreased aromatic matter, as indicated by decreasing  $\text{UV}_{254}$  and SUVA value about 23% and 28%, respectively. It seems that permanganate preoxidation caused the breakdown of high molecular weight (MW) organics into low MW ones, as represented by increasing NPDOC about 10%. Further, disinfection by-products formation potential (DBFPF) in terms of trihalomethanes formation potential (THMFP) and haloacetic acid formation potential (HAAP) decreased about 15% and 23%, respectively. HAAFP removal is higher than THMFP removal and that DPBFP removal is consistent with  $\text{UV}_{254}$  and NPDOC removal.

### Introduction

Natural organic matter (NOM) is an extremely complex mixture of organic compounds found in all water sources. NOM in water contains different fractions or constituents, therefore, NOM has a significant impact on water quality during water treatment and in water distribution systems. Preoxidation has been known as an effective way in promoting the coagulation of their organic matter [1,2] and algal cells [3], and its widely used in drinking water treatment. Preoxidation could be conducted by ozone, chlorine, chlorine dioxide, permanganate, it has been reported that peroxidation could change the zeta potential and structure of algae cells and deactivate cell to promote their aggregation [4]. Preoxidation by permanganate also generates manganese dioxides in situ, which can adhere to the cells and promote their settling [5]. However, if chlorine is added as a disinfectant during water treatment, it will form disinfectant by-products (DBPs), which have been found to be carcinogenic, hepatotoxic, or mutagenic [6,7].

In conventional drinking water treatment process, preoxidation with chlorine before coagulation may be practiced. It is used for  $\text{NH}_4^+\text{-N}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  oxidation and control of biological growth within the treatment plant. However, chlorine may also react with NOM to form DBPs. Alternative pre-oxidants, such as ozone,  $\text{ClO}_2$ , and  $\text{KMnO}_4$ , may be used.  $\text{KMnO}_4$  has the advantage of easy application and lower initial costs. Further,  $\text{KMnO}_4$  may have some effects on NOM removal. For example: its

reducing product,  $MnO_{2(s)}$ , was reported to have adsorption power for humic acid [8] and some low AMW organics [9], and facilitate their removal in the following coagulation process.

In this study, NOM surrogates and DBPFP was used to characterize the NOM in the source water and treated water from permanganate preoxidation. At the same time, the removal of NOM surrogates and DBPFP by various permanganate dosage were also examined.

### 9 Material and method

The raw water used from Tai Hu Reservoir in Kinmen Island, Taiwan. The reservoirs is the main source of drinking water production for the population in those region.

Preoxidation was conducted with a six-paddle gang stirrer jar test apparatus (Phipps & Bird, Richmond, Virginia, USA). First, various dosage of  $KMnO_4$  (Merck, Germany) is 0.25, 0.5, 1, 1.8, 2.7, 4 (mg/L), was added into the water-filled jar under 100 rpm rapid mixing and duration for rapid mixing was 3 min. The speed was then reduced to 35 rpm for 16 min., followed by quiet settling for 30 min. The supernatants were collected, and filtered through 0.45  $\mu m$  filter (cellulose acetate, Toyo Roshi, Japan) before further analysis.

The source water and treated water were analyzed for general physicochemical characteristics, such as nonpurgeable dissolved organic carbon (NPDOC), ultraviolet absorbance at 254 nm ( $UV_{254}$ ), based on procedures from Standard Methods [10]. NPDOC was measured by the combustion-infrared method using total organic carbon analyzer (Model TOC-500, Shimadzu, Kyoto, Japan).  $UV_{254}$  was measured using UV/vis spectrophotometer (Model U-2001, Hitachi, Japan) with a 1-cm quartz cell. SUVA values is obtained by dividing the  $UV_{254}$  absorbance value by the concentration of NPDOC.

Four species of trihalomethanes, namely chloroform, dichlorobromomethane, dibromochloromethane, and bromoform, were measured by the purge and trap packed-column gas chromatographic method using a gas chromatograph (Model 3400 GC, Varian, USA) equipped with a purge and trap module (Model LCS-2000, Tekmar USA) and an electron capture detector.

The measurement of nine species of haloacetic acids, namely monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid, tribromoacetic acid, bromochloroacetic acid, dichlorobromoacetic acid, and dibromochloroacetic acid, basically involved liquid-liquid extraction with methyl tertiary butyl ether (MTBE) and esterification with diazomethane prior to GC-ECD analysis.

### 13 3. Results and discussion

#### 3.1. Characteristic of source water

The general water quality parameters of both samples were shown in Table 1. Taihu has neutral pH and low turbidity and significantly low of alkalinity. Organic matters analysis supported that effluent of slow sand filter relatively less aromatic as presented by SUVA less than 2 L/mg-m and much humic substances.

**Table 1.** Characteristic of organic matter in effluent slow sand filter

NPDOC (mg/L)	Water Quality			DBPs Concentration	
	$UV_{254}$ ( $cm^{-1}$ )	SUVA (L/mg-m)	Alkalinity (mg/L as $CaCO_3$ )	THMFP ( $\mu g/L$ )	HAAFP ( $\mu g/L$ )
4.19	0.058	1.38	35	911.64	257.77

DBPFP and SUVA have shown consistency in characterizing organic matter in source water, which

SUVA as a bulk optical proxy primarily capture the aromatic character of DOM but not the potentially relevant aliphatic components [7]. Also, it confirmed that hydrophobic carbon, which is rich in aromatic content and conjugated double bonds, is the major THM and HAA precursor in natural waters [11,12]. While, aliphatic structures has important role in THM formation than in HAA formation [13]. Therefore, it may be concluded that Taihu has significantly THMFP due to higher proportion of aliphatic components, in addition to aromatic components.

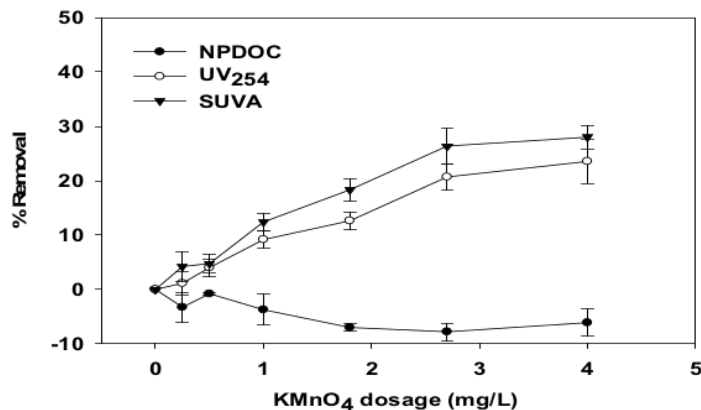
#### 12 Effect of $\text{KMnO}_4$ preoxidation on removal efficiency of organic matters

The effect of the various  $\text{KMnO}_4$  dosage on the NOM removal in effluent slow sand filter were measured by NPDOC,  $\text{UV}_{254}$  and SUVA (Table 2), as well as with the percentage removal of organic matter after preoxidation (Figure 1). As preoxidant dosage increased, the NPDOC increased, while  $\text{UV}_{254}$  decreased in-line with decreasing SUVA removal.

**Table 2.** NOM surrogates concentration under various  $\text{KMnO}_4$  dosage

$\text{KMnO}_4$ (mg/L)	Organic Matter Concentration		
	NPDOC (mg/L)	$\text{UV}_{254}$ ( $\text{cm}^{-1}$ )	SUVA (L/mg-m)
0	4.21±0.01	0.058±0.00	1.38±0.0
0.25	4.24±0.11	0.057±0.00	1.32±0.03
0.5	4.34±0.01	0.056±0.00	1.31±0.02
1.0	4.36±0.12	0.053±0.00	1.21±0.02
1.8	4.50±0.02	0.051±0.00	1.13±0.02
2.7	4.53±0.05	0.046±0.00	1.02±0.04
4.0	4.56±0.09	0.044±0.00	0.99±0.03

The oxidation mechanisms through organic matter caused breaking down of higher organic molecular weight to lower molecular weight [2,4]. Breaking down high molecular weight is indicated by removal of  $\text{UV}_{254}$  and SUVA, which referred to degradation of aromatic compound. Organic matter degradation product in term of low molecular weight is indicated by increasing of NPDOC, which means another organic compound was formed during preoxidation. It seems that preoxidation, which transformed organic fractions, is ineffective in removing organic compound. However, permanganate oxidation followed by coagulation was found to cause a greater reduction, or preoxidation is used to enhanced coagulation to remove organic matter [1,2].



**Figure 1.** Percentage removal of NOM in various  $\text{KMnO}_4$  dosage

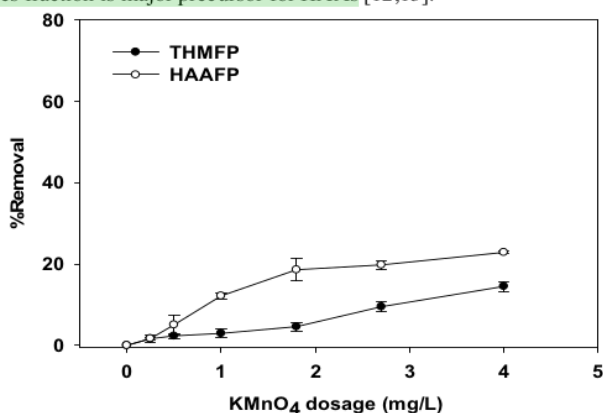
### 3.3. Effect of $KMnO_4$ preoxidation on removal efficiency of DBPFP

Table 3 shows DBPFP values in effluent of slow sand filter before and after preoxidation. The results obtained that the application of preoxidation can achieve a removal of THMFP and HAAFP less than 10% and 20%, respectively (Figure 2).

**Table 3.** DBPFP concentration under various  $KMnO_4$  dosage

$KMnO_4$ (mg/L)	DBPFP Concentration ( $\mu\text{g/L}$ )	
	THMFP	HAAFP
0	911.64 $\pm$ 0.14	257.77 $\pm$ 0.82
0.25	896.82 $\pm$ 3.79	253.36 $\pm$ 0.33
0.5	890.59 $\pm$ 5.02	245.50 $\pm$ 0.84
1.0	884.91 $\pm$ 9.71	226.35 $\pm$ 1.83
1.8	869.81 $\pm$ 9.16	209.80 $\pm$ 0.94
2.7	825.00 $\pm$ 11.10	206.73 $\pm$ 2.53
4.0	779.47 $\pm$ 11.27	198.75 $\pm$ 0.98

It could be explained that aromatic carbon were oxidized by  $KMnO_4$  preoxidant. HAA precursors are aromatic in nature, while THM may have relatively more aliphatic in addition to aromatic. Therefore, it is concluded that THMFP has a higher value than HAAFP. Also, HAAFP removal is higher than THMFP removal and that DBPFP removal is consistent with  $UV_{254}$  and NPDOC removal. It has been conjectured that the aliphatic biopolymer fraction is the major precursor for THMs, while the aromatic humic substances fraction is major precursor for HAAs [12,13].



**Figure 2.** Removal DBPFP as a function of  $KMnO_4$  dosage in effluent slow sand filter

## 4. Conclusions

Increasing permanganate dosage could decreased aromatic matter, as indicated by decreasing  $UV_{254}$  and SUVA value about 23% and 28%, respectively. It seems that permanganate preoxidation caused the breakdown of high molecular weight (MW) organics into low MW ones, as represented by increasing NPDOC about 10%. Further, disinfection by-products formation potential (DBPFP) in terms of trihalomethanes formation potential (THMFP) and haloacetic acid formation potential (HAAFP) decreased about 15% and 23%, respectively. HAAFP removal is higher than THMFP removal and that DBPFP removal is consistent with  $UV_{254}$  and NPDOC removal.

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