

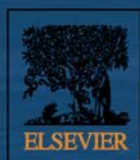
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Could wastewater analysis be a useful tool for China?



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Comparison of different combined treatment processes to address the source water with high concentration of natural organic matter during snowmelt period

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ABSTRACT

The source water in one forest region of the Northeast China had very high natural organic matter (NOM) concentration and heavy color during snowmelt period. The efficiency of five combined treatment processes was compared to address the high concentration of NOM and the mechanisms were also analyzed. Conventional treatment can hardly remove dissolved organic carbon (DOC) in the source water. KMnO_4 pre-oxidization could improve the DOC removal to 22.0%. Post activated carbon adsorption improved the DOC removal of conventional treatment to 28.8%. The non-sufficient NOM removal could be attributed to the dominance of large molecular weight organic matters in raw water, which cannot be adsorbed by the micropore upon activated carbon. O_3 + activated carbon treatment are another available technology for eliminating the color and UV_{254} in water. However, its performance of DOC removal was only 36.4%, which could not satisfy the requirement for organic matter. The limited ozone dosage is not sufficient to mineralize the high concentration of NOM. Magnetic ion-exchange resin combined with conventional treatment could remove 96.2% of color, 96.0% of UV_{254} and 87.1% of DOC, enabling effluents to meet the drinking water quality standard. The high removal efficiency could be explained by the negative charge on the surface of NOM which benefits the static adsorption of NOM on the anion exchange resin. The results indicated that magnetic ion-exchange resin combined with conventional treatment is the best available technology to remove high concentration of NOM.

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Introduction

Natural organic matter (NOM) is a complex mixture of organic materials and presents ubiquitously in all natural water, particularly surface waters (Matilainen et al., 2010). NOM affects many esthetic aspects of water quality, such as annoying color, taste and odor problems (Matilainen et al., 2002, 2011). Moreover, NOM has been noted as a major contributor to the disinfection byproduct (Krasner et al., 2006; Liu et al., 2012). Thus, NOM has been regarded as a focus in water industry throughout the world.

Depending on the biogeochemical cycles of the surrounding environments, the properties of NOM differ considerably in waters of different origins (Nissinen et al., 2001; Fabris et al., 2008). The quantity and quality of NOM, which change seasonally due to the change of weather, vegetation and humification, have impacts on the selection, design and operation of water treatment processes (Chen et al., 2008).

The practical drinking water treatment processes for NOM removal include enhanced coagulation, activated carbon adsorption, O_3 + granular activated carbon (GAC) or biological activated carbon

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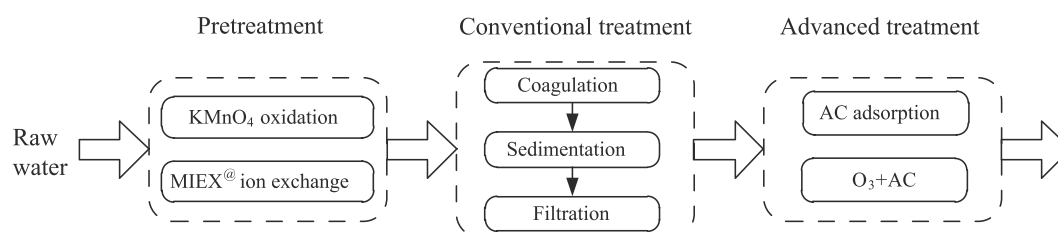


Fig. 1 – Relationship of the water treatment units for the NOM removal.

(BAC) treatment process, ion exchange, and membrane filtration. Among these treatment processes, enhanced coagulation is the most widely-applied method (Jiang and Graham, 1996; Zhan et al., 2010). Its efficiency for DOC removal varies from 20% to 60% (Jacangelo et al., 1995). Activated carbon (AC) is effective in adsorbing the hydrophobic compounds with small molecular weight (MW) (Drikas et al., 2009). AC has the dissolved organic carbon (DOC) removal efficiency of $30\% \pm 12\%$ in one pilot test (Chen et al., 2007). Currently, ozone and BAC treatment process is more and more popular for NOM and other organic matter removal. In the ozone and BAC treatment, NOM could be oxidized and probably decomposed into smaller compounds by ozone and then biodegraded during biological activated carbon filtration (Boere, 1992; Chen et al., 2011; Qian et al., 2013). Anion exchange resin has high efficacy of combining or adsorbing the negatively charged NOM (Humbert et al., 2005). One promising anion exchange technology, i.e. magnetic ion-exchange resin (MIEX), has a high capacity for NOM and could precipitate quickly with aid of magnetic force, which benefits the application in water treatment plants (Gan et al., 2013; Kingsbury and Singer, 2013).

The source water in one forest region of the Northeast China suffered a high concentration of NOM, which was chosen as the raw water in this study. The NOM in the source water was brought by the snowmelt water flowing through the forest. Heavy brown color was observed due to the high load of NOM. Meanwhile, the concentration of organic matter is over 10 mg/L. The conventional treatment processes could hardly handle the NOM-rich source water. Besides, the temperature of snowmelt water was close to ice point, which restrained the biodegradation in the BAC process. Thus, the investigation of process choice is requested by the local water company.

This study focused on the following objectives: (1) Characterizing of the properties of NOM in the source water. The MW distribution, surface charge distribution and fluorescence were determined for NOM property characterization. (2) Comparing the removal efficiency of different water treatment processes and giving the suggestions for process selection. (3) Investigating the mechanisms of the different treatment processes for the NOM removal.

1. Materials and methods

1.1. Source water

The source water was sampled from the Gulian River, which runs through the Great Xing'an Mountain Forest, Heilongjiang Province in Northeast China. The snowmelt water brought high concentration NOM from the forest and took it into the river. The water sample was stored in ice box and delivered to the lab in Tsinghua University, Beijing within two days. The working temperature (12°C) is lower down to approach the real temperature of snowmelt water ($2\text{--}4^\circ\text{C}$). Actually, the influence of temperature on water treatment process could be described by the Arrhenius law, i.e.

$$k = Ae^{-(E_a/RT)}$$

Table 1 – Combined water treatment processes for the NOM removal.

Process name	Processes combination	Parameters and notes
Conventional treatment process (CTP)	Coagulation and sedimentation	Simulated with a jar tester ^a . Coagulation was conducted by 300 r/min fast mixing for 1 min and slow agitation at 60, 45, and 30 r/min for 5 min, respectively. Coagulant: polymeric aluminum chloride (PAlC) 3 mg/L measured as Al
	Filtration	Sedimentation time: 30 min
KMnO ₄ enhanced conventional process	KMnO ₄ pre-oxidation	Simulated with the 0.45 μm membrane filter
		Dosage: 2.0 mg/L
		Contact time: 30 min
MIEX enhanced conventional process	CTP	Same as above mentioned
	MIEX pretreatment	MIEX resin ^b dosage: 10 mL/L (6 g/L in dry resin); contact time: 30 min
Conventional and activated carbon (AC) process	CTP	Same as above mentioned
	AC adsorption	Same as above mentioned
		Simulated with 80 mg/L of powder activated carbon (milled F400 activated carbon with size of 200 mesh); contact time: 120 min
Conventional and O ₃ + AC process	CTP	Same as above mentioned
	O ₃	O ₃ ^c dosage: 1 mg/L; contact time: 10 min
	AC adsorption	Simulated with 80 mg/L of powder AC; contact time: 120 min

^a The jar tester (model ZR4-6) was made by Zhongrun Water Industry Technology Development Company, Shenzhen, China.

^b MIEX[®] resin was made by Orica Watercare, Melbourne, Australia.

^c Ozone was produced onsite by a DHX-SS-1G ozone generator, Jiujiu Electronic Chemical Engineering and Technology Company, Harbin, China.

where, k is the react rate constant; A is the Arrhenius factor; E_a is the activation energy; T is the temperature and R is the constant parameter.

The difference of reciprocal of temperature, i.e. $1/277$ vs. $1/285$ is negligible. Thus, our experiment can still present reliable results of treatment processes to address the snowmelt water.

This source water was very impressive for its heavy brown color of 79 Hazen units (HU), as measured by a Hach Lico500 chroma meter (Hach, Loveland, Colorado, USA). The high UV_{254} absorbance, 0.506, also indicated the existence of large load of organic matter. The concentrations of DOC and chemical oxygen demand for potassium permanganate (CODMn) of water sample were as high as 15.5 and 14.0 mg/L, respectively.

1.2. Treatment processes

The conventional treatment and its combinations with $KMnO_4$ pre-oxidation, MIEX pretreatment, AC adsorption or O_3 + AC advanced treatment process were compared to treat the sampled source water. The flowchart of these combined processes is shown in Fig. 1. The parameters of these treatment processes are summarized in Table 1.

1.3. Water quality parameters and analytical methods

The MW distribution of NOM in the water sample was determined by a high performance size exclusion chromatography (HPSEC) (Li et al., 2010). The mobile phase consisted of a 70/30 (V/V) mixture of 10 mmol/L NH_4HCO_3 and methanol. The mobile phase delivered as a flow rate of 1.00 mL/min and a 20 μ L of sample solution was injected into the analytical column. The column effluent was monitored by the UV absorbance at 254 nm. The column was calibrated with molecular mass standards comprising polystyrene sulfonic acid sodium salt standards (PSS, Sigma-Aldrich, Louis, Missouri, USA) from 210 Da to 32 kDa. The characteristic of MW distributions indicates the removal efficiency by different treatment processes, and provides the basis for the selection of treatments and their combinations.

Excitation–Emission Matrix (EEM) spectra or three-dimensional fluorescence were measured using an F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). The EEM spectrum of Milli-Q water was subtracted from EEM spectra to remove Raman scatter peaks. The EEM data were quantified following the fluorescence regional integration (FRI) technique (Chen et al., 2003). The EEM spectra were divided into five regions, each representing some specific components of DOC (Table 2).

Titration of NOM was performed using a Metrohm 905 Titrando (Metrohm, Herisau, Switzerland). A known concentration of NOM was prepared in carbon dioxide-free water and equilibrated in NaCl solution of 0.01 mol/L at 25°C. A known amount of NaOH was added to adjust the solution pH to 11.5. Then, the solution was titrated with 0.05 mol/L of HCl solution until pH reach 3. A blank titration was also performed under the same conditions. The concentration of acidic groups on NOM surface could be calculated by the difference between blank and NOM titration results, based on the assumption that NOM would be fully protonated at pH 3 (Newcombe and Drikas, 1997; Bjelopavlic et al., 1999).

Color was determined by Hach Lico500 chroma meter (Hach, Loveland, Colorado, USA) with a 50 mm path length cell with a platinum/cobalt standard. This gave a direct reading of the color in Hazen units. UV_{254} was measured by ultraviolet–visible spectrophotometer (UV-2700, Shimadzu, Kyoto, Japan). A total organic carbon (TOC) analyzer (TOC 5000, Shimadzu, Kyoto, Japan) were used to measure the DOC concentration of the water samples. The specific ultraviolet absorbance (SUVA), which is a surrogate parameter for hydrophobicity of organic matter, was determined by dividing the value of UV_{254} absorbance to the DOC concentration.

2. Results and discussion

2.1. Characteristic of NOM in source water

The heavy color (79 HU) and high DOC concentration (15.5 mg/L) demonstrated the typical water quality profile of humic-rich water (Table 2). The high SUVA value (3.26) indicated that the aquatic organic matter contained more unsaturated bonds and presented higher aromaticity (Matilainen et al., 2010).

The EEM result or the fluorescence of NOM in raw water is demonstrated in Fig. 2. It is obvious that a prominent fluorescence peak exists in regions III and V, taking 69.6% of the total fluorescence intensity. This result evidenced the dominant existence of humic substances (including humic acid in region V and fulvic acid in region III) in raw water.

The titration result illustrated the distribution of charge upon the NOM surface, as demonstrated in Fig. 3. Under normal operation range (pH 6–8) in drinking water treatment, NOM presents fairly high density of negative charge, from 0.0022 to 0.0056 mmol/mg. The negative charge could be attributed to the ionization of carboxyl groups. With the increase of pH value, the density of negative charge increased sharply between pH 8–11, which was due to the ionization of phenol group on the NOM (Edzwald and Tobiasson, 1999). The surface charge density will

Table 2 – Categories of pollutants for different three-dimensional fluorescence regions.

Regions	Excitation wavelength (nm)	Emission wavelength (nm)	Probable category for pollutants
I	200–250	250–330	Aromatic protein I
II	200–250	330–380	Aromatic protein II
III	200–250	380–550	Fulvic acids
IV	250–400	250–380	Dissolved microbial metabolics
V	250–400	380–550	Humic acids

significantly influence the fate of NOM during drinking water treatment process, as further discussed in Section 2.3.3.

The MW distribution of NOM in raw water is presented in Fig. 4. The majority of NOM formed a large bump in the curve which covered the MW from 1 to 10 kDa. A small bump of curve was contributed by the organic compounds around 500 Da to 1 kDa. In sum, the percentages of large MW fraction (>3 kDa), moderate MW fraction (1–3 kDa) and small MW fraction (<1 kDa) were 48%, 42% and 11%, respectively.

2.2. Comparison of NOM removal by different combined treatment processes

The efficiency of five combined treatment processes was compared according to the removal of bulk water quality parameters, i.e. color, UV₂₅₄ and DOC, as summarized in Table 3. The conventional treatment had a very limited efficiency on NOM removal, and only 1.5% of DOC was removed. Thus, the enhancement by pre-oxidation, ion exchange or advanced treatment is extraordinarily necessary. Meanwhile, the conventional treatment had moderate removal of color and UV₂₅₄ (34.2% and 23.5%, respectively). The KMnO₄ enhanced conventional treatment improved the DOC removal efficiency to 22.0%. The removal efficiencies of UV₂₅₄ and color were also increased. The MIEX enhanced conventional treatment had an outstanding performance of NOM, color and UV₂₅₄ removal. The DOC concentration was decreased from 15.5 to 2.0 mg/L with a high removal of 87.1%. The color and UV₂₅₄ removal were as high as 96.0% and 96.2%, respectively. It is surprising that activated carbon can only improve the DOC removal to 28.8% even with high dosage of 80 mg/L. The fairly low efficiency declined the application of powdered activated carbon (PAC) to tackle with humic-rich source water.

The addition of ozone in above process eliminated 89.7% of the color and 92.4% of the UV₂₅₄ in raw water, which indicated the destruction of chromogenic groups and unsaturated bonds in NOM compounds. However, this advanced treatment only improved DOC removal from 1.5% to 36.4%, which is still not qualified for NOM removal. This result could be explained by the

limited ozone dosage of 1 mg/L that cannot mineralize the organic completely. Moreover, the SUVA value decreased sharply after ozonation from 2.53 (effluent of conventional processes) to 0.53, which indicated that the residual organic lost the unsaturated bonds and was given the more polar functional groups, such as carboxyl or hydroxyl. The increased polarity made it more recalcitrant to AC adsorption. Based on the comparison of treatment efficiency, the MIEX treatment is highly recommended for its excellent performance in the removal of humic organics.

2.3. Mechanisms of NOM removal by different treatment processes

2.3.1. Change of MW distribution of NOM

The MW distribution of the organic in different treatment processes and units effluents are illustrated in Fig. 4. The integral peak area of different MW range after treatment is summarized in Table 4. The conventional treatment could remove 32% of large molecule with MW over 3 kDa. The change of the larger molecular NOM concentration could also be reflected in the variation of UV₂₅₄, color, and the MW distribution. The KMnO₄ enhanced conventional treatment improved the organic removal in the whole MW range. The organic compounds with larger MW (>3 kDa) was the most preferentially removed after KMnO₄ pre-oxidation. The NOM removal efficiency increased from 32% to 51%. In general, AC adsorption preferred to adsorb the organics with MW less than 500 Da due to the size matching of micropore on the AC surface. The majority of organic matter in this source water had a larger MW over 1 kDa. Thus, AC adsorption could not play an effective role in removing NOM in this water. MIEX pretreatment almost completely eliminated the organic matter in the range of >3 kDa, 1–3 kDa and part of the organic matter smaller than 1 kDa. This indicated that the negative charge existed ubiquitously on surface of organic matters with the whole MW spectrum. This result also testified that MIEX pretreatment was not MW-selective for NOM removal and can significantly remove the organics.

Ozonation is effective to destroy/transform the unsaturated bonds, which was also evidenced by the UV₂₅₄ removal of 89.7% as shown in Table 3. Actually, the HPSEC method uses 254 nm as the organic matter indicator. Thus, the MW distribution after

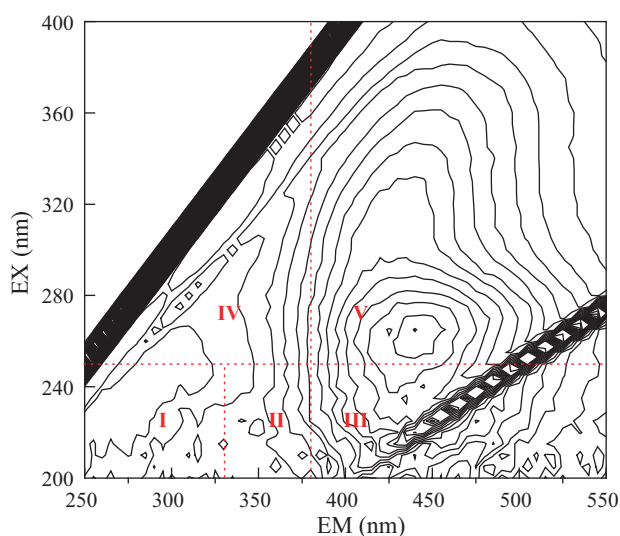


Fig. 2 – Fluorescence analysis of organic matters in raw water.

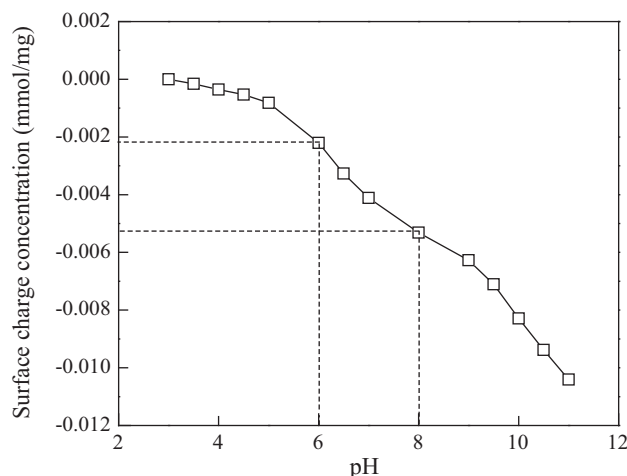


Fig. 3 – Surface charge concentration of the raw water.

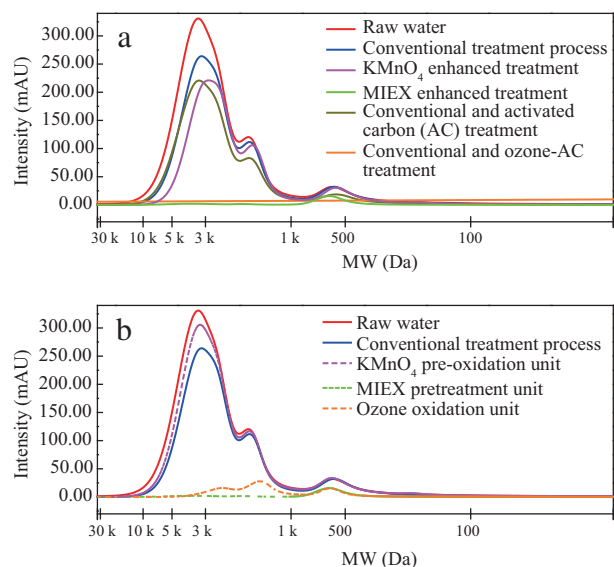


Fig. 4 – Comparison of MW distribution of NOM after the combined treatment processes (a) and the unit process (b).

ozonation matched the UV_{254} removal quite well. However, DOC removal by ozonation and AC adsorption was not high as the UV_{254} decrease since many organic compounds did not have UV absorbance at 254 nm.

As illustrated in Fig. 5, NOM had a wide spectrum of UV absorbance covering ultraviolet C (UVC, 200–280 nm), ultraviolet B (UVB, 280–315 nm) to ultraviolet A (UVA, 315–400 nm). After ozonation, the absorbance at UVA, UVB and part of UVC was destroyed or transformed almost completely while the absorbance below 250 nm remained, indicating the incomplete mineralization of organic. However, MIEX pretreatment is non-selective for eliminating the NOM with absorbance of full UV spectrum, confirming that MIEX is more reliable process for this humic-rich water. Besides, this result indicates that 254 nm or larger wavelength is not suitable for HPSEC to detect the MW distribution for ozonated water.

2.3.2. Change of humic substances by different combined processes
This source water was rich in humic substances. It is well known that humic substances have unique fluorescence in the EEM spectrum. Thus, the change of fluorescence intensity in the region III and V could be used to illustrate the removal of humic substances by different combined processes.

As shown in Fig. 6, conventional treatment process had very limited removal of humic substances. The pretreatment

of KMnO_4 only enhanced the conventional process by 16.2% of the fluorescence removal. MIEX could significantly remove the humic substance by 92.1%, which is close to the DOC removal. The post activated carbon adsorption could further improve fluorescence to 28.0%. It could be concluded that ozonation could significantly diminish the fluorescence. Although conventional and O_3 + AC process had similar removal of fluorescence and UV_{254} absorbance as the MIEX enhanced conventional process, the DOC removal was much lower. The result implies that destruction of fluorescence or UV absorbing functional groups is much easier than the mineralization by oxidants. The physical treatment processes, such as ion-exchange or adsorption are more reliable options than chemical oxidation processes when DOC requirement is more challenging.

2.3.3. Mechanism of NOM removal by different unit processes

The mechanism of NOM removal by coagulation includes a combination of charge neutralization, entrapment and adsorption by floc. The charge-driven mechanism has been concluded to be more important for NOM removal according to previous studies (Zhao et al., 2009; Bond et al., 2010). As shown in Fig. 3, the NOM in source water existed as negative charged in pH 3–11. However, the surface charge density of source water, 0.004 mmol/mg at pH 7, was smaller than the waters reported before, which is 0.017 mmol/mg (Bjelopavlic et al., 1999). The fairly low surface charge density would restrain the CTP performance, which explains the low NOM removal by coagulation in this study.

The KMnO_4 pre-oxidation would improve the NOM removal efficiency of conventional treatment (Zhang et al., 2009). The mechanism lies in two parts. On one hand, MnO_2 , the reduction product of KMnO_4 , can enhance the coagulation efficiency and the NOM removal. On the other hand, KMnO_4 pre-oxidation could directly oxidize and remove part of NOM.

MIEX is a kind of strong anion exchange resin. The dominant fraction of NOM in this water, i.e. humic acid and fulvic acid presented a certain amount of negative charge in the experimental pH, which benefits the removal by ion exchange. Please note that ion exchange is much more powerful than coagulation. In addition, the MIEX resin has a diameter of 150–180 μm , 2–5 times smaller than conventional ion-exchange resin, which endows the resin large surface area. These properties increased the treatment efficiency greatly (Drikas et al., 2011; Nguyen et al., 2011).

AC is a non-polar or weakly-polar adsorbent widely used in drinking water treatment (Uyak et al., 2007). The efficiency of AC adsorption depends on the simultaneously matching of polarity and size. Although humic acid or fulvic acid in this source water

Table 3 – Comparison of NOM removal by different combined treatment processes.

Process	DOC		UV_{254}		Color		SUVA
	Value (mg/L)	Removal	Value	Removal	Value (HU)	Removal	
Raw water	15.5	/	0.506	/	79	/	3.26
Conventional treatment processes	15.3	1.5%	0.387	23.5%	52	34.2%	2.53
KMnO_4 enhanced conventional processes	12.1	22.0%	0.328	35.2%	46	41.8%	2.71
MIEX enhanced conventional processes	2.0	87.1%	0.020	96.0%	3	96.2%	1.00
Conventional and AC processes	11.1	28.8%	0.262	48.2%	34	57.0%	2.37
Conventional and O_3 + AC processes	9.9	36.4%	0.052	89.7%	6	92.4%	0.53

Table 4 – Integral area of different MW range after treatment.

Process	>3 kDa		1–3 kDa		<1 kDa	
	Peak area	Removal	Peak area	Removal	Peak area	Removal
Raw water	5531	/	5005	/	1249	/
Conventional treatment processes	3751	32%	4479	11%	1141	9%
KMnO ₄ enhanced processes	2718	51%	3736	25%	921	26%
MIEX enhanced processes	0	100%	20	100%	310	75%
Conventional and AC processes	3262	41%	3073	39%	688	45%
Conventional and O ₃ + AC processes	0	100%	458	91%	475	62%

is more non-polar, which favors the AC adsorption, the size of NOM is too large to be adsorbed by the AC micropore. For organic matter with MW over 500 Da, the mesopore or macropore is needed to hold it. However, the volume of mesopore or macropore is quite small on AC. Therefore, the NOM removal of AC is limited in this situation.

O₃ + AC treatment was widely used to provide high quality water (Qian et al., 2013). Ozonation could destroy and transform the NOM into smaller chemicals, increase the polarity and also improve the biodegradability (Chen et al., 2007). However, the low temperature in snowmelt water restrains the biological activity in GAC filter. As mentioned above, AC adsorption only presents moderate removal of this NOM due to the non-matching of large MW with micropore size.

2.3.4. Feasibility analysis of MIEX enhanced process

In this investigation, we tried several treatment process combinations to address this humic-rich water. We applied the technically available parameters of real water treatment plants, such as the mixing strength, sedimentation time, the dosages of coagulant, ozone, KMnO₄ and MIEX resin. The AC adsorption is the one of difference with real GAC filter. To make up this difference, we used a large dosage of i.e. 80 mg/L to give a maximum performance of AC filter. It is very obvious that the AC adsorption is not capable for this source water and MIEX has more outstanding performance than other options.

Moreover, the cost of MIEX treatment is now comparable to that of O₃–GAC process. The cost of O₃–GAC process is

0.30 CNY/m³ water, including the construction, reagent, electricity, human resource, maintenance, and depreciation (Zhou, 2006). According to the operation report of one water treatment plant using MIEX process in China, the cost of MIEX treatment process is about 0.19 CNY/m³ water (Sun et al., 2012). Another publication on one pilot test gave the cost of about 0.30 CNY/m³ water (Li et al., 2011).

Another concern about MIEX process is the regeneration operation. Actually, MIEX process has been applied in many countries and China for many years (Drikas et al., 2011; Wang et al., 2012). The regeneration with sodium chloride solution is very reliable and robust. The MIEX resin will be soaked into the regeneration tank filling with the saturated salt solution. The wastewater after regeneration will be diluted with backwashing water from filter and settling tank to meet the discharge standard for wastewater in China.

In all, MIEX enhanced conventional process is a competent and feasible process to address this NOM-rich source water.

3. Conclusions

The extremely high concentration of natural organic matter in the source water during snowmelt period brought a big challenge to drinking water treatment. Five kinds of combined treatment processes were compared to address the NOM-rich source water during snowmelt period. The result indicated that MIEX combined with conventional treatment is the best available technology to remove high concentration of organic matter.

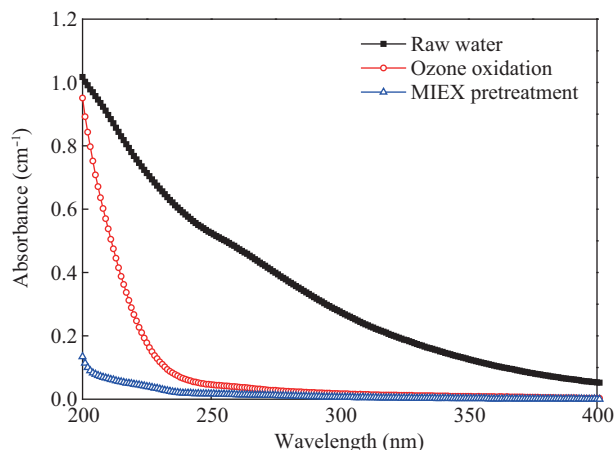


Fig. 5 – UV spectrum scanning of effluents by different treatments.

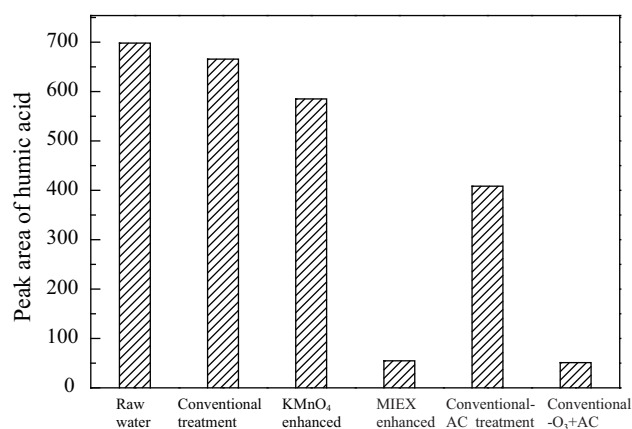


Fig. 6 – Fluorescence change of humic substances after different treatment processes.

Conventional treatment can hardly remove DOC in the source water and its efficiencies on color and UV₂₅₄ were just 34.2% and 23.5%. The KMnO₄ pre-oxidation could improve the DOC removal to 22.0%, which is still not qualified. Post AC adsorption improved the DOC removal of conventional treatment to 28.8%. The non-sufficient NOM removal could be attributed to the dominance of large MW organic matters in raw water, which cannot be adsorbed by the micropore upon AC. O₃ + AC treatment are another available technology for eliminating the color and UV₂₅₄ in water. However, its performance of DOC removal was only 36.4%, which could not satisfy the requirement for organic matter. MIEX combined with conventional treatment could remove 96.2% of color, 96.0% of UV₂₅₄ and 87.1% of DOC in this snowmelt source water, enabling effluents to meet the drinking water quality standard. The high removal efficiency could be explained by the negative charge on the surface of NOM.

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